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May 1985

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

May 1985

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.



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1 SUMMARY

UREA (NH_2CONH_2)

White granules or prills, or clear liquid.

SYNONYMS

Carbamide, Carbonyldiamine, Carbonyl Diamide, Carbamimidic Acid

TRADE NAMES

Prespersion, 75 Urea, Ureophil, Urevert, Aquadrate

IDENTIFICATION NUMBERS

UN No. No hazard label required; CAS No. 57-13-6; OHM-TADS No. 7216943; STCC No. Not required

GRADES & PURITIES

Solid: Technical grade (prills), fertilizer grade (prills or granules), 95 percent and higher urea; 99.7 percent urea contains 46 percent by weight N_2

Liquid: 50-80 percent aqueous solutions

IMMEDIATE CONCERNS

Fire: Not combustible.

Human Health: Relatively nontoxic material.

Environment: Harmful to aquatic life in high concentrations.

PHYSICAL PROPERTY DATA

State (15°C , 1 atm): solid

Boiling Point: decomposes before boiling

Melting Point: 133°C

Flammability: noncombustible, decomposes to ammonia gas above 133°C

Specific Gravity: 1.335 ($20^\circ\text{C}/4^\circ\text{C}$)

Solubility (in water): 51.6 g/100 g (20°C)

Behaviour (in water): sinks and mixes; no reaction

ENVIRONMENTAL CONCERNS

Urea is toxic to aquatic life and microorganisms at concentrations above 10 000 mg/L, and to domestic animals at doses above 500 mg/kg.

HUMAN HEALTH

No TLV* or IDLH established.

Exposure Effects

Contact: Causes redness and irritation to skin and eyes.

IMMEDIATE ACTION**Spill Control**

Restrict access to spill site. Notify manufacturer. Stop the flow and contain spill, if safe to do so. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible; most firefighting agents can be used on fires involving urea.

COUNTERMEASURES**Emergency Control Procedures in/on**

Soil: If spilled in solid form, shovel into containers and cover. Construct barriers to contain solutions or divert to impermeable holding area. Remove material by manual or mechanical means. Absorb small amounts of liquid spill with natural or synthetic sorbents, shovel into containers and cover.

Water: Contain by damming, water diversion or natural barriers. Remove and treat contaminated liquids.

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Granular white solid or clear liquid (Sherritt MSDS)
Usual shipping state(s)	Solid: in granule or prill form (Olin PD 1981; Sherritt MSDS) Liquid: aqueous solutions
Physical state at 15°C, 1 atm	Solid
Melting point	132.7°C (Olin PD 1981; Ullmann 1975)
Boiling point	Decomposes before boiling (Olin PD 1981)
Decomposition temperature	135°C (Kirk-Othmer 1983)

Densities

Density	1.3230 g/mL (20°C), 1.147 g/mL (saturated solution at 20°C) (Kirk-Othmer 1983)
Specific gravity	1.335 (20°/4°C) (Sherritt MSDS)
Bulk density	0.74 g/cm ³ (Kirk-Othmer 1983)

Fire Properties

Flammability	Noncombustible solid (Olin PD 1981)
Decomposition temperature	135°C (Kirk-Othmer 1983)
Decomposition products	Biuret, ammonia and cyanuric acid (Merck 1976)

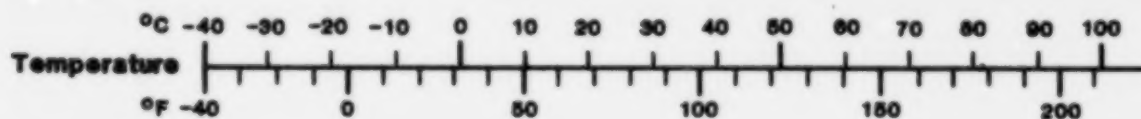
Other Properties

Molecular weight of pure substance	60.06 (CRC 1980)
Constituent components of typical commercial grade	98 percent urea, 1 percent formaldehyde, 1 percent biuret (H ₂ NCOHHCONH ₂) (Sherritt MSDS)
Refractive index	1.484 (CRC 1980) 1.3535 (5 N solution, 35°C) (Chao 1967)
Viscosity	1.78 mPa·s (46 percent solution, 20°C) (CRC 1980) 1.81 mPa·s (melt at 137°C) (Ullmann 1975) 1.90 mPa·s (saturated solution at 20°C) (Kirk-Othmer 1983)

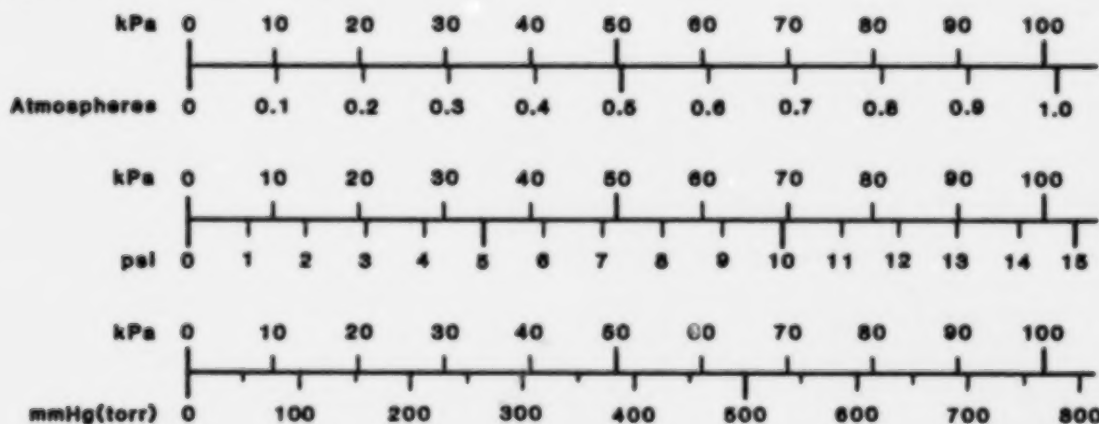
Vapour pressure	1.73 kPa (20°C), 5.33 kPa (40°C) (saturated solutions in water) (Kirk-Othmer 1983)
Latent heat of fusion	15.1 kJ/mole (at melting point) (Kirk-Othmer 1983; Ullmann 1975)
Latent heat of sublimation	87.9 kJ/mole (25°C) (Lange's Handbook 1979)
Heat of formation	-333.7 kJ/mole (25°C) (Sussex 1977)
Entropy	105.5 kJ/(mole·K) (Ullmann 1975)
Ionization potential	9.7 eV (Debies 1974)
Heat of solution	-15.1 kJ/mole (20°C) (Perry 1973) -14.1 kJ/mole (25°C) (Ullmann 1975)
Heat capacity	
constant pressure (Cp)	80.5 J/(mole·°C) (solid at 20°C) (Ullmann 1975) 86 J/(mole·°C) (0°C) (Kirk-Othmer 1983)
Diffusivity	1.37×10^{-5} cm ² /s (in water 20°C) (Perry 1973)
pH of aqueous solution	7.2 (10 percent solution) (Merck 1976)
Log ₁₀ octanol/water partition coefficient	-1.09 (Hansch and Leo 1979)
Dipole moment	4.56, 3.5 (22°C) (Chao 1967)
Dielectric constant	86.1 (3 N solution at 20°C) (Chao 1967)
Solubility	
In water	51.6 g/100 g solution (20°C) (Kirk-Othmer 1983)
In other common materials	Very soluble in methanol and ethanol. Soluble in acetic acid and pyrimidine. Insoluble in diethyl ether, chloroform and benzene (CRC 1980) Solubility in methanol is 22 g/100 g solution; in ethanol, 5.4 g/100 g solution (Ullmann 1975)
Azeotropes	Forms azeotrope with water (67.5 percent by mass) which freezes at -11.5°C

UREA

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm $\approx$ 1 mg/L

Energy (heat) 1 kJ = 1 000 J

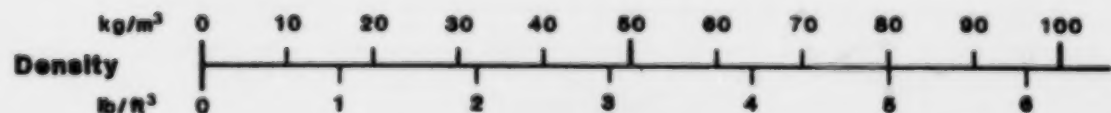
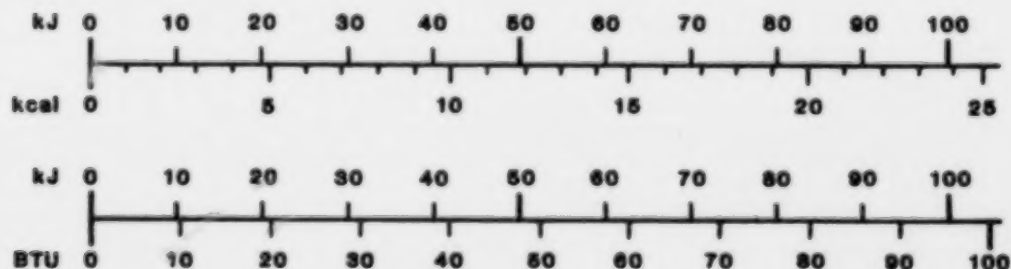


FIGURE 1

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SOLUBILITY IN WATER vs TEMPERATURE

Reference: KIRK-OTHMER 1983

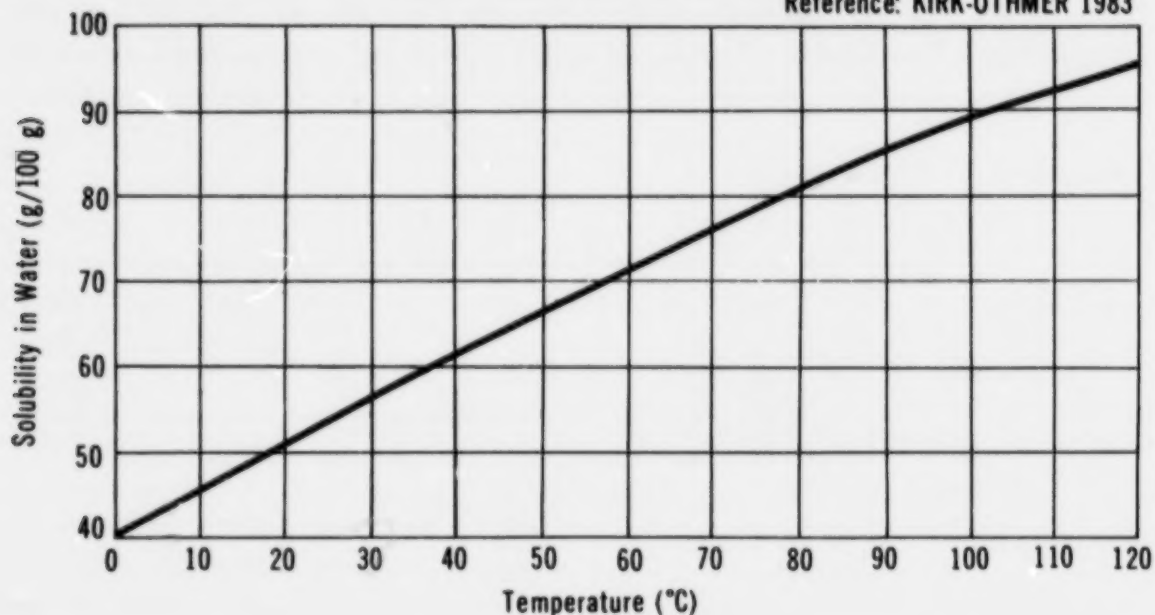
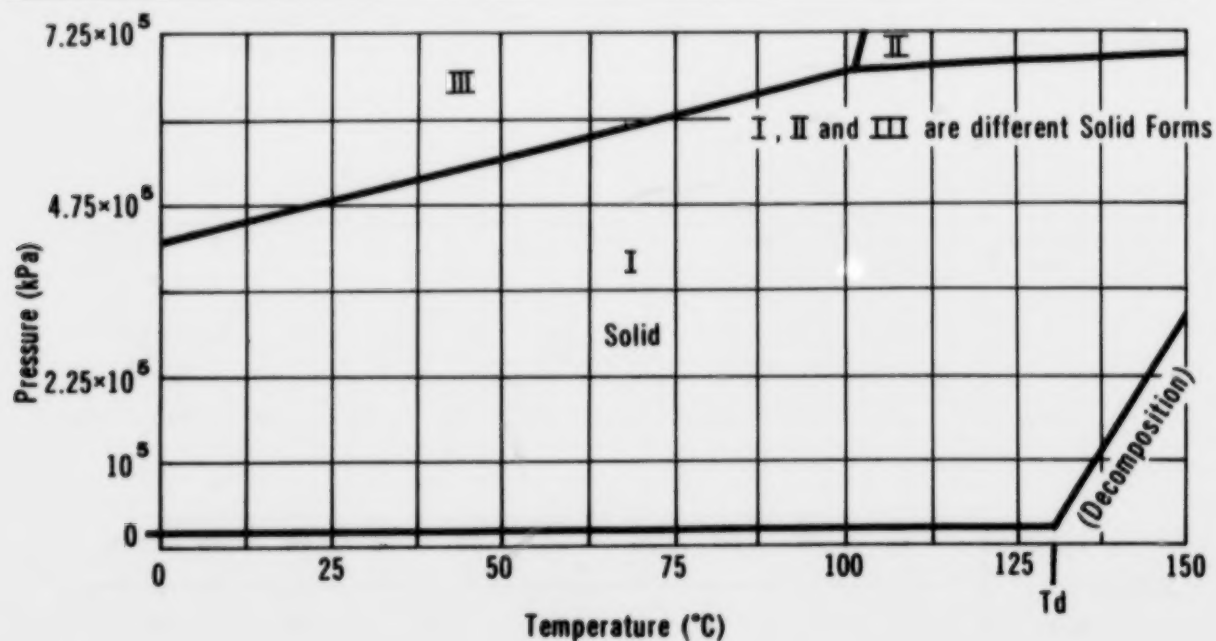


FIGURE 2

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PHASE DIAGRAM

UREA

DENSITY OF AQUEOUS SOLUTIONS

Reference: CHAO 1967

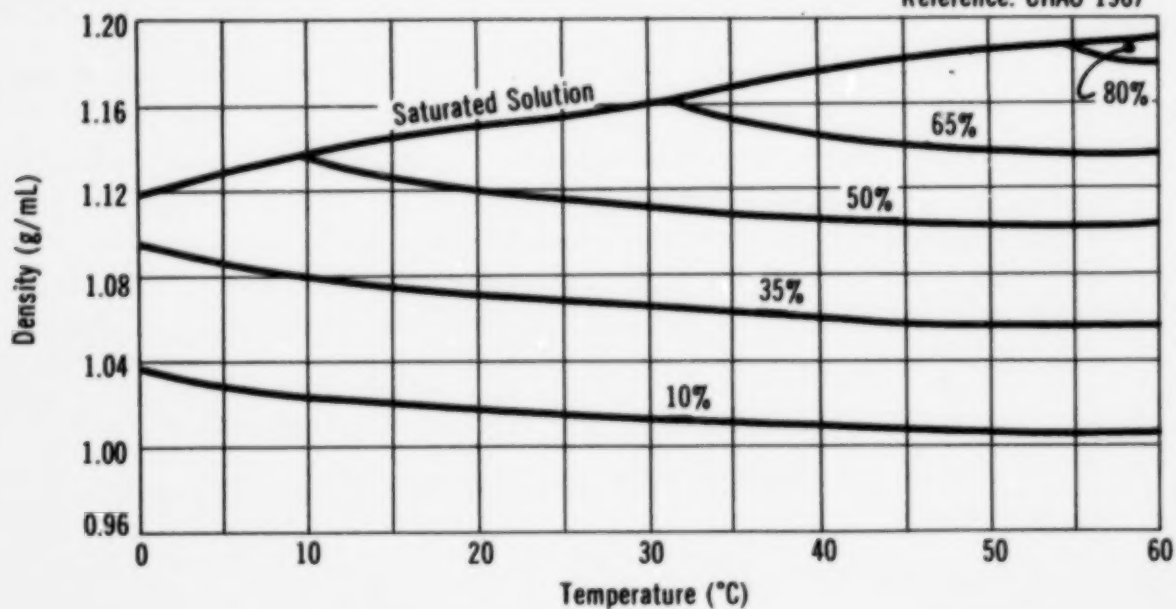
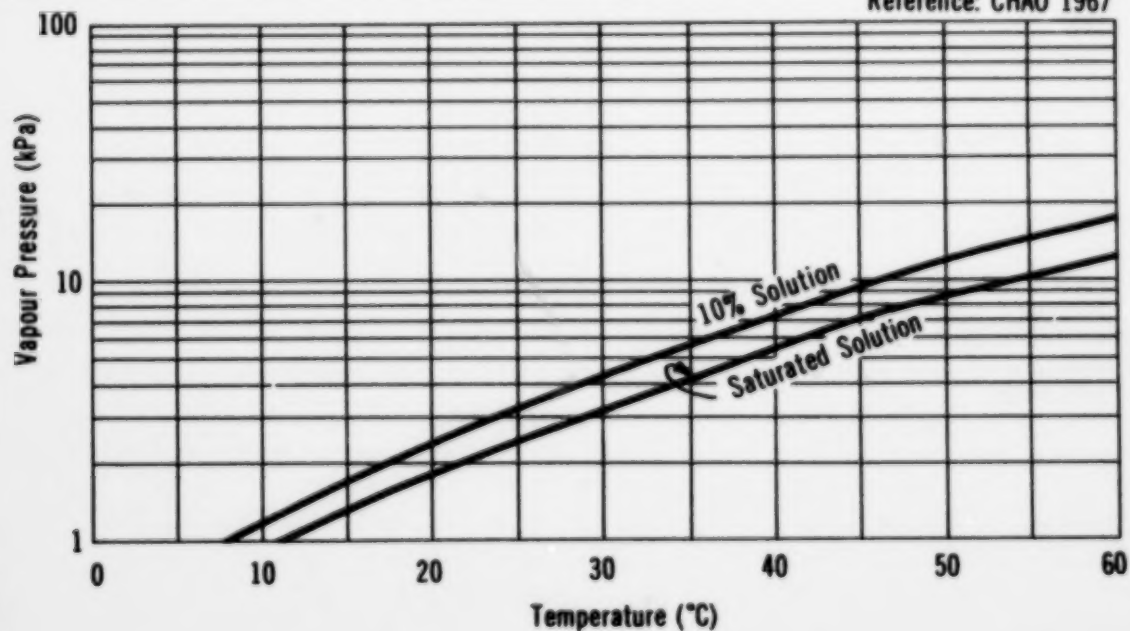


FIGURE 4

UREA

VAPOUR PRESSURE OF SOLUTIONS

Reference: CHAO 1967



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Sherritt 1982; Cyanamid 1982; CCPA 1984)

Urea is sold as a solid or liquid in a number of grades. Liquid urea is sold in 50-80 percent aqueous solutions. Solid urea (produced in grades containing up to 99 percent urea) is sold in the following grades: regular fertilizer grade, granulated or prilled urea containing less than 1.5 percent biuret; special grade, prilled, for special fertilizer applications, containing less than 0.3 percent biuret; technical grade, prilled; and prilled or micropilled feed grade. Note: Most solid grades contain 0.5-1.0 percent biuret unless otherwise noted. Higher amounts of biuret (>2 percent) are detrimental to plant growth. Some urea may contain 0-1 percent formaldehyde.

3.2 Domestic Manufacturers (Corpus 1983; CBG 1980; Scott 1979)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Canadian Fertilizers
P.O. Box 1300
Medicine Hat, Alberta
T1A 7N1
(403) 527-8887

Nitrochem Inc.
2055 Peel Street, Suite 800
Montreal, Quebec
H3B 2X8
(514) 849-9222

C-I-L. Inc.
P.O. Box 200, Station A
90 Sheppard Avenue East
North York, Ontario
M2N 6H2
(416) 226-6110

Sherritt Gordon Mines Ltd.
Box 28, Commerce Court West
Toronto, Ontario
M5L 1B1
(416) 363-9241

Cominco
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

Simplot Chemical Co. Ltd.
P.O. Box 940
Brandon, Manitoba
R7A 6A1
(204) 728-5701

Cyanamid Canada Inc.
2255 Sheppard Avenue East
Willowdale, Ontario
M2J 4Y5
(416) 498-9405

3.3 Other Suppliers (CBG 1980; Corpus 1983; Scott 1979)

Arliss Chemical Co. Inc.
325 Hymus Blvd.
Pointe-Claire, Quebec
H9R 1G8
(514) 694-2170

BASF Canada Ltd.
5850 Cote de Liesse
Montreal, Quebec
H4T 1C1
(514) 341-5411

Canada Colours and Chemicals Ltd.
80 Scarsdale Road
Don Mills, Ontario
M3B 2R7
(416) 924-6831

Coté Chemicals Inc.
111 Bombardier Park
Chateauguay Centre, Quebec
J6J 3X0
(514) 691-6260

Esso Chemical Canada
Division of Imperial Oil Ltd.
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Harrison & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

International Chemical Canada Ltd.
P.O. Box 385
Brampton, Ontario
L6V 2L3
(416) 453-4234

Mallinckrodt Canada Inc.
600 Delmar Avenue
Pointe-Claire, Quebec
H9W 1E6
(514) 695-1220

Nitrochem Inc.
2055 Peel Street
Suite 800
Montreal, Quebec
H3B 2X8
(514) 849-9222

Shefford Chemicals Ltd.
1028 Principale
Granby, Quebec
J2G 8C8
(514) 378-0125

United Co-operatives of Ontario
(Captive)
151 City Centre Drive
Mississauga, Ontario
L5A 3A4
(416) 270-3560

3.4 Major Transportation Routes

Current Canadian production of urea is located primarily in Alberta, at Medicine Hat, Carseland, Fort Saskatchewan and Calgary. Other production facilities are in Ontario, at Courtright, Maitland and Niagara Falls, and in Manitoba, at Brandon. The product is shipped by box cars, tank cars, tank trucks or flatbed trucks.

3.5 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Canadian Fertilizers, Medicine Hat, Alta.	435
C-I-L, Courtright, Ont.	160
Cominco, Calgary, Alta.	70
Cominco, Carseland, Alta.	435
Cyanamid Canada, Niagara Falls, Ont.	90
Nitrochem, Maitland, Ont.	45*
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	80
Simplot Chemical, Brandon, Man.	142
TOTAL	1457
Domestic Production (1982)	1230.5
Imports (1982)	101
TOTAL SUPPLY	1331.5

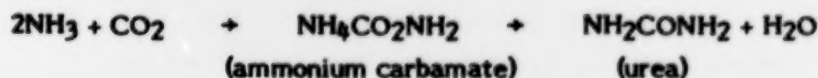
* Plant moth-balled in 1983.

C-I-L is planning to expand its plant in Courtright, Ontario, by 134 kt/yr (CCP 1982b). Sherritt Gordon (Fort Saskatchewan, Alberta) is expanding its urea capacity by 220 kt/yr; Simplot (Brandon, Manitoba) is expanding by 115 kt/yr (Corpus 1983).

3.6 Manufacture of Urea (Kirk-Othmer 1983; Sullivan 1982; FKC 1975)

3.6.1 General. Urea is made by the reaction of anhydrous ammonia and carbon dioxide to form ammonium carbamate, and the decomposition of the latter to urea.

3.6.2 Manufacturing Process. An excess of liquid ammonia and gaseous carbon dioxide (usually at a ratio of 2.5:1) are fed into a reactor with a small amount of water:



The reaction is conducted at a pressure of about 20 000 kPa and a temperature of 180–200°C, in the presence of a metal catalyst. The conversion to ammonium carbamate is nearly quantitative; conversion to urea is in the 50–70 percent range, depending on the process.

The reaction mixture is then conducted to a series of decomposers where the pressure is reduced and unconverted ammonium carbamate is decomposed by heat. The resulting ammonia and carbon dioxide, as well as the excess of ammonia originally charged, are ultimately recycled.

Urea solids are produced by flash distillation or vacuum crystallization of water from the urea solution; prills are formed by dropping molten urea down a spray tower. Anti-caking ingredients may be added at this stage to facilitate handling and storage.

3.7 Major Uses in Canada (Corpus 1983)

Urea is used in direct fertilization, forest fertilization, nitrogen (and nitrogen-phosphate) solutions, fertilizer mixtures, animal feeds, and U-F resins. In 1982, 44 percent of domestic production was exported, 37 percent was used for direct fertilization and 8 percent was used for nitrogen solutions.

3.8 Major Buyers in Canada (Corpus 1983; CCPA 1984)

Agricultural Chemicals, London, Ont.
 Borden Chemical, Toronto, North Bay, Ont.
 Canada Packers, Toronto, Ont.
 Coopérative Fédérée du Québec, Montréal, Qué.
 William Houde, Laprairie, Que.
 MacMillan Bloedel, Vancouver, B.C.
 Monsanto Canada, LaSalle, Que.
 Nitrochem Inc., Montreal, Que.
 Northwood Pulp, Prince George, B.C.
 Nutrite Inc., Toronto, Ont.
 Pacific Logging, Victoria, B.C.
 Perkins Adhesives, Valleyfield, Que.
 Reichhold, North Bay, Ont.
 St. Regis Alberta, Hinton, Alta.
 United Cooperatives of Ontario, Mississauga, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. A large portion of the material is shipped as a solid by rail or truck, or as a solution by rail.

4.1.1.1 Railway cars. Railway tank cars used for transporting solutions are not regulated. Commonly used tank cars are described in Table 2. As indicated in Table 2, tankers may be unloaded from top or bottom depending on the class of car selected. Cars may be unloaded from the top or bottom by pump or by gravity from the bottom (PC 1982). A typical 111A60W1 tank car is illustrated in Figure 5; details associated with this car are given in Table 3.

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Test pressure 414 kPa (60 psi). Urea resins only.
111A60W1 (IL)	Same as 111A60W1 except interior-lined for urea solutions.
111A60ALW1	Aluminum fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Safety valve (242 kPa) (35 psi) or safety vent (414 kPa) (60 psi). Bottom outlet or washout optional. Test pressure 414 kPa (60 psi). For urea solutions and resins.
111A100W6	Alloy (stainless) steel fusion-welded tank without dome. Insulated or uninsulated. 2% minimum outage. Gauging device. Safety valve (518 kPa) (75 psi) or safety vent (690 kPa) (100 psi). Bottom outlet or washout optional. Test pressure 690 kPa (100 psi). Urea resins only.

* Canadian Transport Commission and Department of Transportation (U.S.)

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RAILWAY TANK CAR - CLASS 111A60W1

(Reference - TCM 1979, RTDCR 1974)

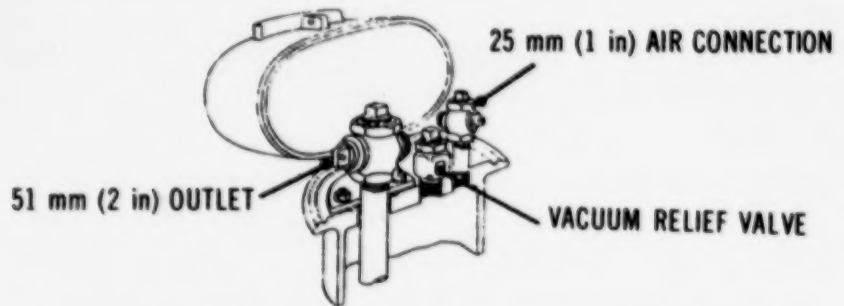
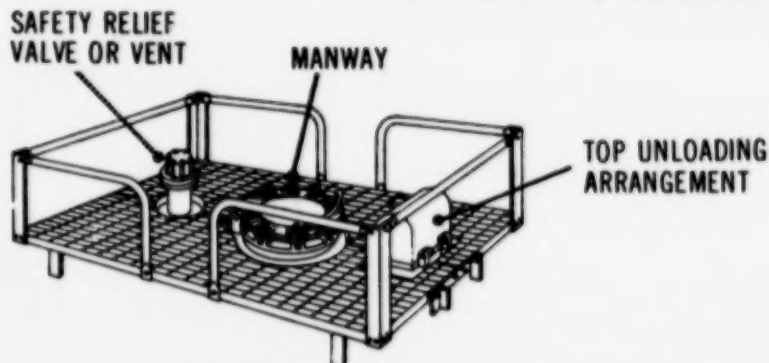
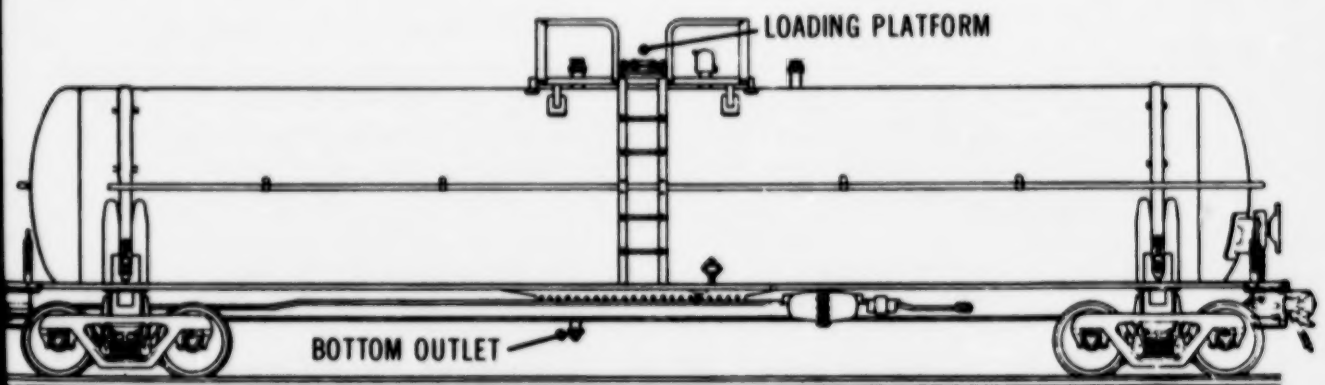
**Detail of top unloading arrangement****Detail of loading platform****Illustration of tank car layout**

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

	Tank Car Size (Imp. Gal.)					
Description	16 700		17 200		20 000	
<u>Overall</u>						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L	(20 000 gal.)
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg	(85 800 lb.)
Car weight - max.	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
<u>Tank</u>						
Material	steel		steel		steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
<u>Approximate Dimensions</u>						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centres	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2 to 3 m	(8 to 10 ft.)	2 to 3 m	(8 to 10 ft.)	2 to 3 m	(8 to 10 ft.)
Width of grating	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)
<u>Loading/Unloading Fixtures</u>						
<u>Top Unloading</u>						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203 to 356 mm	(8 to 14 in.)	203 to 356 mm	(8 to 14 in.)	203 to 356 mm	(8 to 14 in.)
Air connection	25 to 51 mm	(1 to 2 in.)	25 to 51 mm	(1 to 2 in.)	25 to 51 mm	(1 to 2 in.)
<u>Bottom Unloading</u>						
Bottom outlet	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)
<u>Safety Devices</u>						
	Safety vent or valve					
<u>Dome</u>						
	None					
<u>Insulation</u>						
	Optional					

Solid prill and granular material is transported in covered bulk hopper cars and box cars in bagged form. Hopper cars are gravity or pneumatically unloaded. Capacities vary from 45 to 90 tonnes (PC 1982). Typical hopper cars are illustrated in Figure 6 and described in Table 4. "Cylindrical" hopper cars with specifications similar to the latter are also frequently used.

4.1.1.2 Tank motor vehicles. Solid prill and granular material is transported in bulk form in dump trucks or in pneumatic type trucks in capacities of 18 to 45 tonnes. In bagged form, flatbed trucks are utilized (PC 1982).

Urea solutions are not specifically regulated, but MC311 and MC312 carriers are generally used. Both classes are covered under the Transport Canada TC312 specifications. Such specifications require that cargo tanks unloaded by pressure in excess of 104 kPa (15 psi) be designed and constructed in accordance with the ASME Code (TDGC 1980). Capacities of highway tankers transporting urea solutions vary from 18 to 32 tonnes. Insulated stainless steel tankers usually transport 50-80 percent aqueous solutions (PC 1982).

4.1.2 Packaging. In addition to bulk shipments, urea in prilled and granulated form is also shipped in drums, paper bags and plastic bags (PC 1982).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Two means of off-loading urea solution rail cars are used, top off-loading and bottom off-loading.

Proceed with top off-loading as follows (PC 1982):

- Remove the protective housing from the discharge valve at the top of the car and connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pumping.

Proceed with bottom off-loading as indicated below:

- Connect the unloading line to a 152 mm (6 in.) bottom outlet and open the inside bottom valve by turning the valve handle at the top of the car.
- Off-load the car by gravity or pump.

Prior to off-loading granular and prilled urea, certain chemicals such as urea formaldehyde are often added to control dust (Sherritt MSDS 1978).

4.2.2 Specifications and Materials for Off-loading Equipment. Fully annealed Schedule 40 carbon steel mechanical tubing made to ASTM Specification A53 and then

UREA

COVERED HOPPER CARS - AAR CLASS LO

(Reference - CLC 1974, AAR 1983)

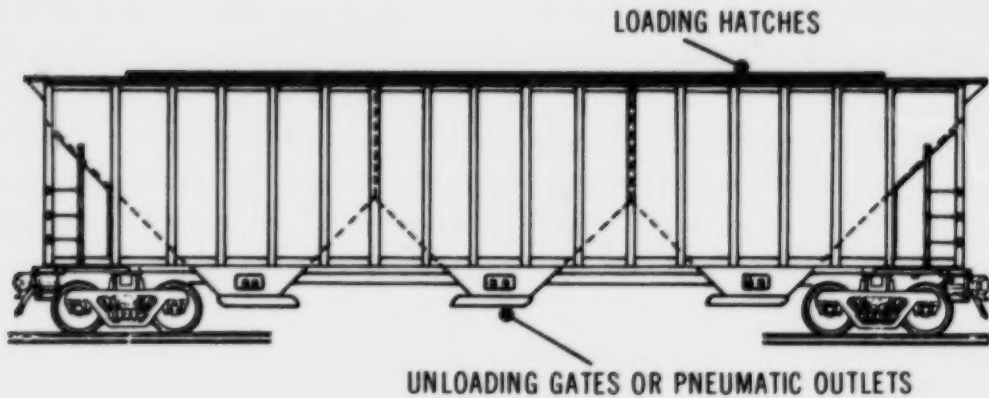
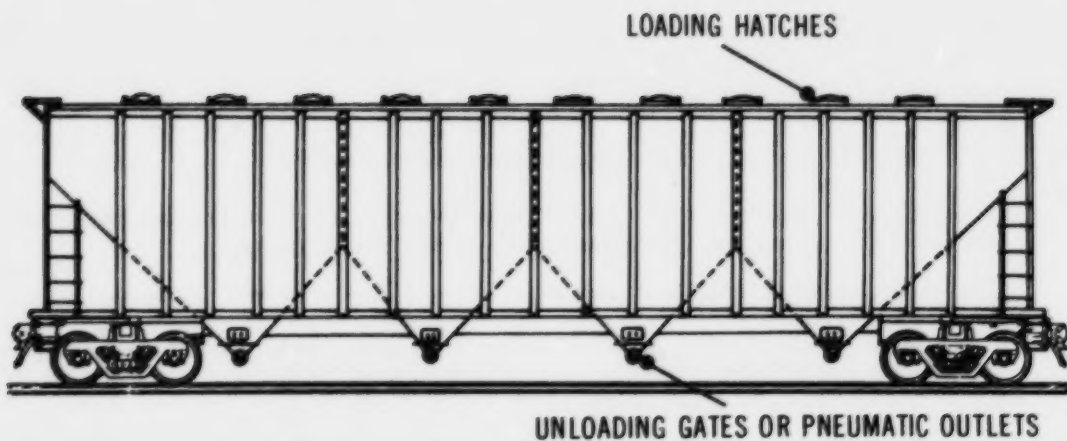
**Typical 3 - Compartment Hopper Car****Typical 4 - Compartment Hopper Car**

TABLE 4 TYPICAL RAILWAY HOPPER CAR SPECIFICATIONS - AAR CLASS LO (CLC 1974)

Description	Hopper Car Size (cu. ft.)	
	5800	4700
<u>Overall</u>		
Nominal capacity	164 m ³ (5800 cu. ft.)	133 m ³ (4700 cu. ft.)
Weight capacity	86 000 kg (190 000 lb.)	89 000 kg (196 000 lb.)
Car weight - empty	45 000 kg (100 000 lb.)	45 000 kg (100 000 lb.)
Car weight - max.	119 000 kg (263 000 lb.)	119 000 kg (263 000 lb.)
<u>Hoppers/Compartments</u>		
Number	4	3
Material	steel	steel
Inside length (typical)	410 cm (160 in.)	460 cm (180 in.)
Inside width (typical)	300 cm (118 in.)	300 cm (118 in.)
Spacing between outlets	4 m (13 ft.)	5 m (15 ft.)
Slope angle	40 to 45°	40 to 45°
<u>Approximate Dimensions</u>		
Coupled length	21 m (68 ft.)	18 m (60 ft.)
Length over strikers	20 m (65 ft.)	17 m (57 ft.)
Length of truck centres	16 m (54 ft.)	14 m (46 ft.)
Clearance height	5 m (15 ft.)	5 m (15 ft.)
Height to top of running board	5 m (15 ft.)	4 m (14 ft.)
Overall width	3.1 m (123 in.)	3.2 m (126 in.)
Inside length	19 m (63 ft.)	17 m (55 ft.)
<u>Loading/Unloading Fixtures</u>		
<u>Loading Hatches:</u>	Cars typically equipped with 4 to 12 loading hatches. Typical dimensions of these are 36 to 61 cm (14 to 24 in.) in diameter or square dimensions.	
<u>Unloading Fixtures:</u>	Equipped with unloading gates at bottom of 36 to 61 cm (14 to 24 in.) square and/or pneumatic unloading connections of 10 to 20 cm (4 to 8 in.) in diameter.	

lined with polyvinylidene chloride (Saran) is recommended for urea solutions at medium temperatures (DPLP 1972). Plain carbon steel pipes and fittings may be used at normal temperatures (PC 1982). Flanged joints of compatible material should be used. The unloading line is usually 51 mm (2 in.) pipe, to suit standard discharge fittings on rail cars.

Flexible bellows-type expansion joints may be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion member molded from tetrafluoroethylene resin (Dow PPS 1972).

Diaphragm valves of cast iron bodies lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (DPLV 1972). Chlorosulphonated polyethylene resin is an adequate gasket material in this service (DPLP 1972).

An all-iron centrifugal pump, close-coupled, is suitable in this service. Stainless steel or Monel are recommended (Cyanamid MSDS 1976).

For handling granular and prilled material, normal solids handling equipment is used (Sherritt MSDS 1978).

4.3 Compatibility with Materials of Construction

The compatibility of urea solutions with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system is briefly described below:

<u>Recommended:</u>	This material will perform satisfactorily in the given application.
<u>Conditional:</u>	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
<u>Not Recommended:</u>	Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Most	23	PE* (DPPED 1967)		
		52	PVDC (DCRG 1978)		
		60	PVC I PVC II (DPPED 1967)		
		93	PP (DCRG 1978)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (Cont'd)		121	PVDF Chlorinated Polyether (DCRG 1978)		
		To operating limit of material	PVC I (MWPP 1978)		
	Solid product	Most	CS (Cyanamid MSDS 1976)		ABS, PE (MWPP 1978)
2. Valves	Most	23	Chlorinated Polyether PVDC SS 316, SS 317 (Cyanamid MSDS 1976)		
3. Pumps	Most	Most	Iron SS (Cyanamid MSDS 1976)		
4. Storage	Most	Most	CS, SS (PC 1982)		
5. Others	Up to 10% or 33%	60	PE, PP POM, NR NBR, IIR EPDM, CR FPM, CSM (GF)	uPVC (GF)	
		60	PVC (TPS 1978)		
		82	PP (TPS 1978)		
		85	CPVC (TPS 1978)		
		121	PVDF (TPS 1978) SBR (GPP)		
	10 to 50%	24 to 100	Glass (CDS 1967)		

* This material has been given a lower rating in a similar application by another reference.

TABLE 6 MATERIALS OF CONSTRUCTION

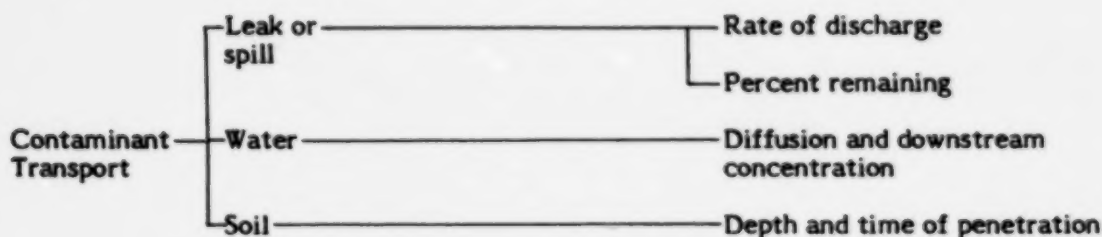
Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Aluminum
	Cast Iron
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
	Iron
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (followed by grade if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (followed by grade)	Stainless Steel
	Tetrafluoroethylene
uPVC	Unplasticized Polyvinyl Chloride

5 CONTAMINANT TRANSPORT

5.1 General Summary

Urea is transported as a solid, in granule or prill form, in covered hopper cars, or as an aqueous solution in tankers. When spilled in water, all forms will dissolve rapidly. When spilled on soil, the liquid form will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Transport of urea toward the water table may be an environmental concern. Because urea is essentially nonvolatile, dispersion in air is not a problem.

Factors considered for the transport of a urea spill in water and soil are shown below:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Urea is transported as solid crystals or pellets or as an aqueous solution. In aqueous form, urea is commonly transported in railway tank cars. While the capacities of the tank cars vary widely, one tank car has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. This size has been used throughout the EnviroTIPS manuals to allow for comparison between different substances.

If a tank car loaded with dilute aqueous solution is punctured on the bottom, all of the contents will drain out by gravity. Higher concentrations of urea solution are

highly viscous or solid at normal temperatures and will not drain by gravity unless the temperature is elevated.

The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the low volatility of urea solution and the fact that tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

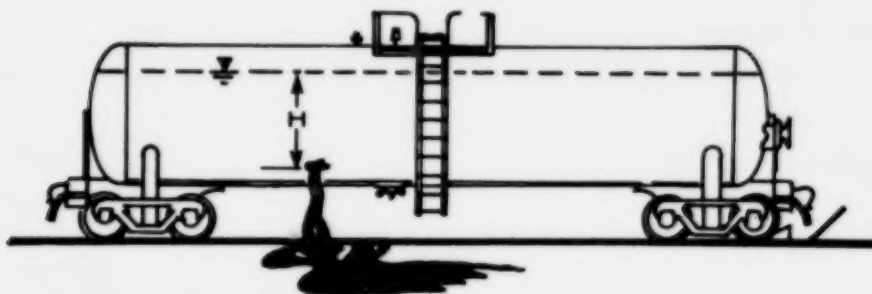


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with a 70 percent aqueous solution of urea has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

FIGURE 8

UREA (70% SOLUTION)

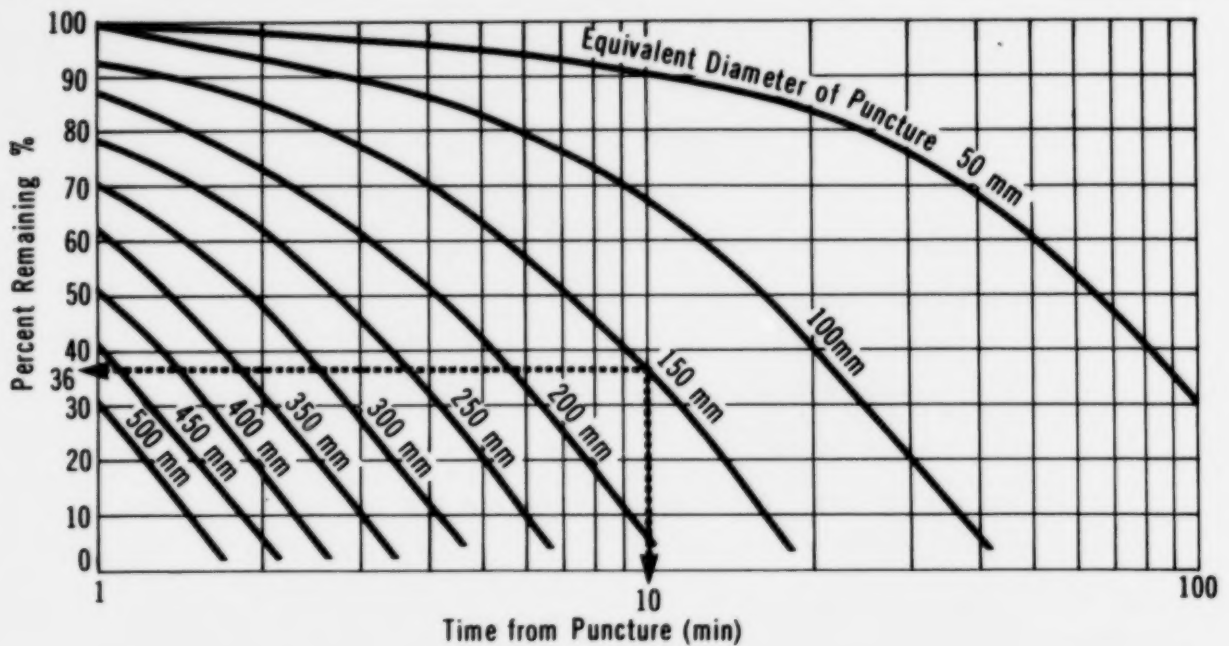
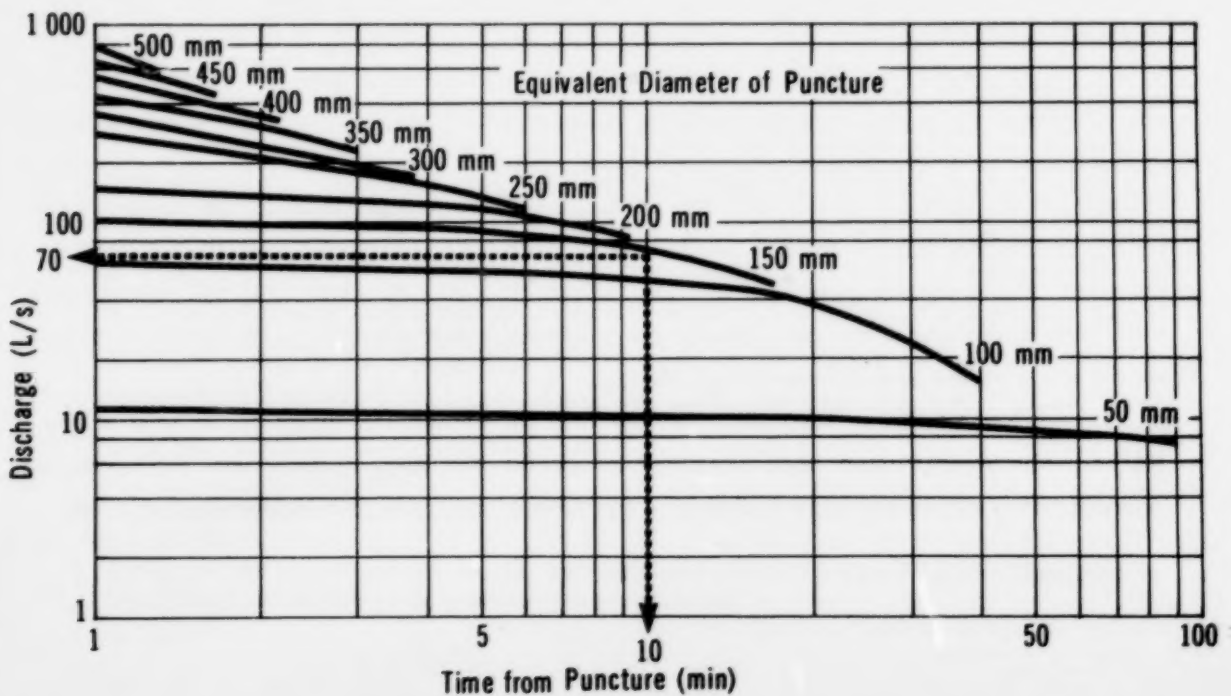
PERCENT REMAINING
VS TIME

FIGURE 9

UREA (70% SOLUTION)

DISCHARGE RATE
VS TIME

Solution to Problem A

- . Use Figure 8
- . With $t=10$ min and $d=150$ mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- . Use Figure 9
- . With $t=10$ min and $d=150$ mm, the instantaneous discharge rate (q) = 70 L/s

5.3 Dispersion in the Air

Because urea is nonvolatile in foreseeable spill circumstances, there is no significant potential for dispersion in air.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, urea will dissolve rapidly. Mixing takes place and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d < 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

- Figure 11: time versus distance for a range of average stream velocities
- Figure 12: hydraulic radius versus channel width for a range of stream depths
- Figure 13: diffusion coefficient versus hydraulic radius for a range of average stream velocities
- Figure 14: α^* versus diffusion coefficient for various time intervals
- Figure 15: α versus δ^* for a range of spill sizes
- Figure 16: maximum concentration versus δ for a range of river cross-sectional areas

Lakes or Still Water Bodies

- Figure 17: volume versus radius for the hazard zone for a range of lake depths
- Figure 18: average concentration versus volume for the hazard zone for a range of spill sizes.

The flowchart in Figure 10 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 11 through 18) are described in the following subsections.

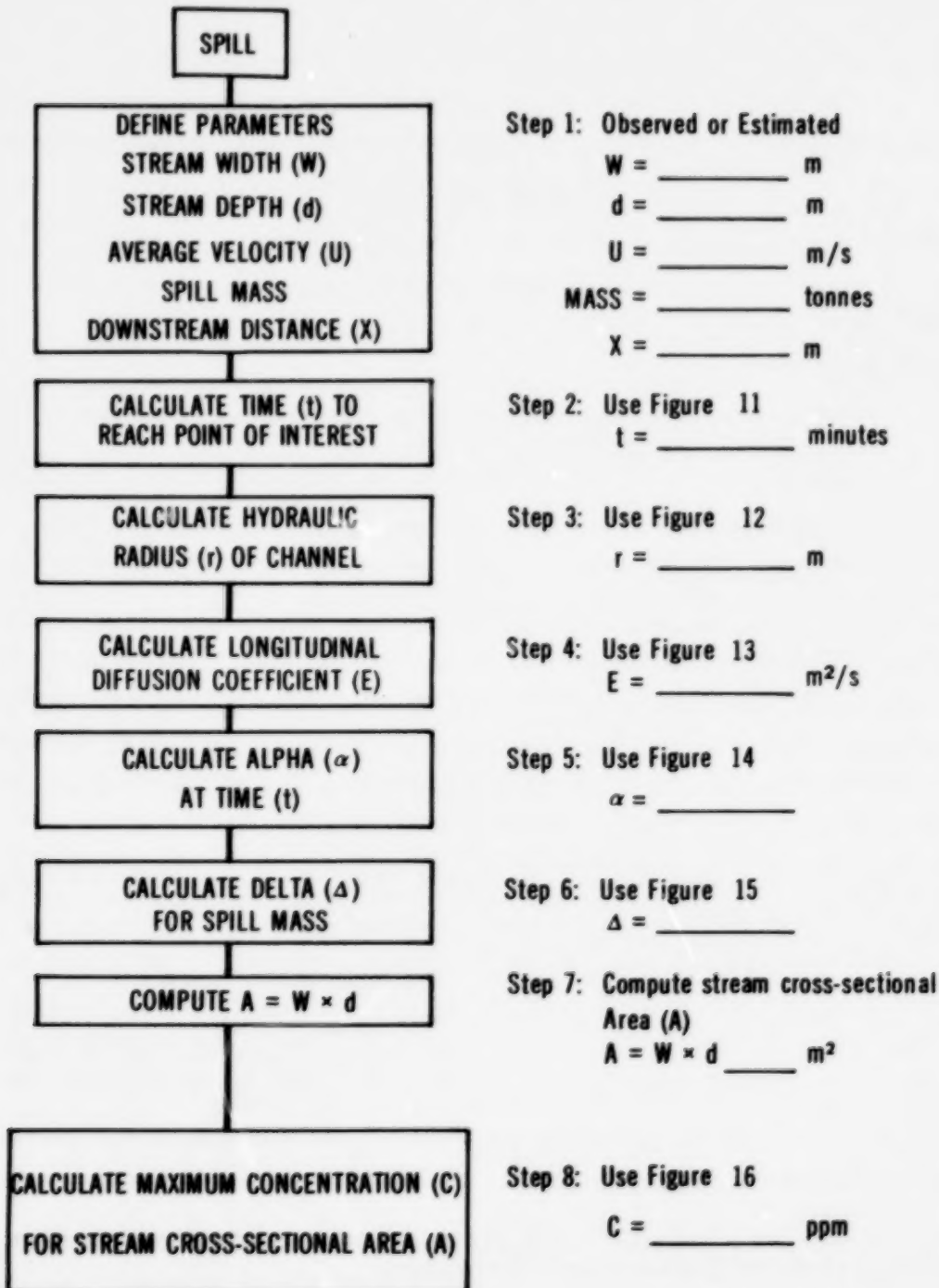
5.4.2.1 Nomograms for non-tidal rivers.

Figure 11: Time versus distance. Figure 11 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 11.

Figure 12: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 12 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

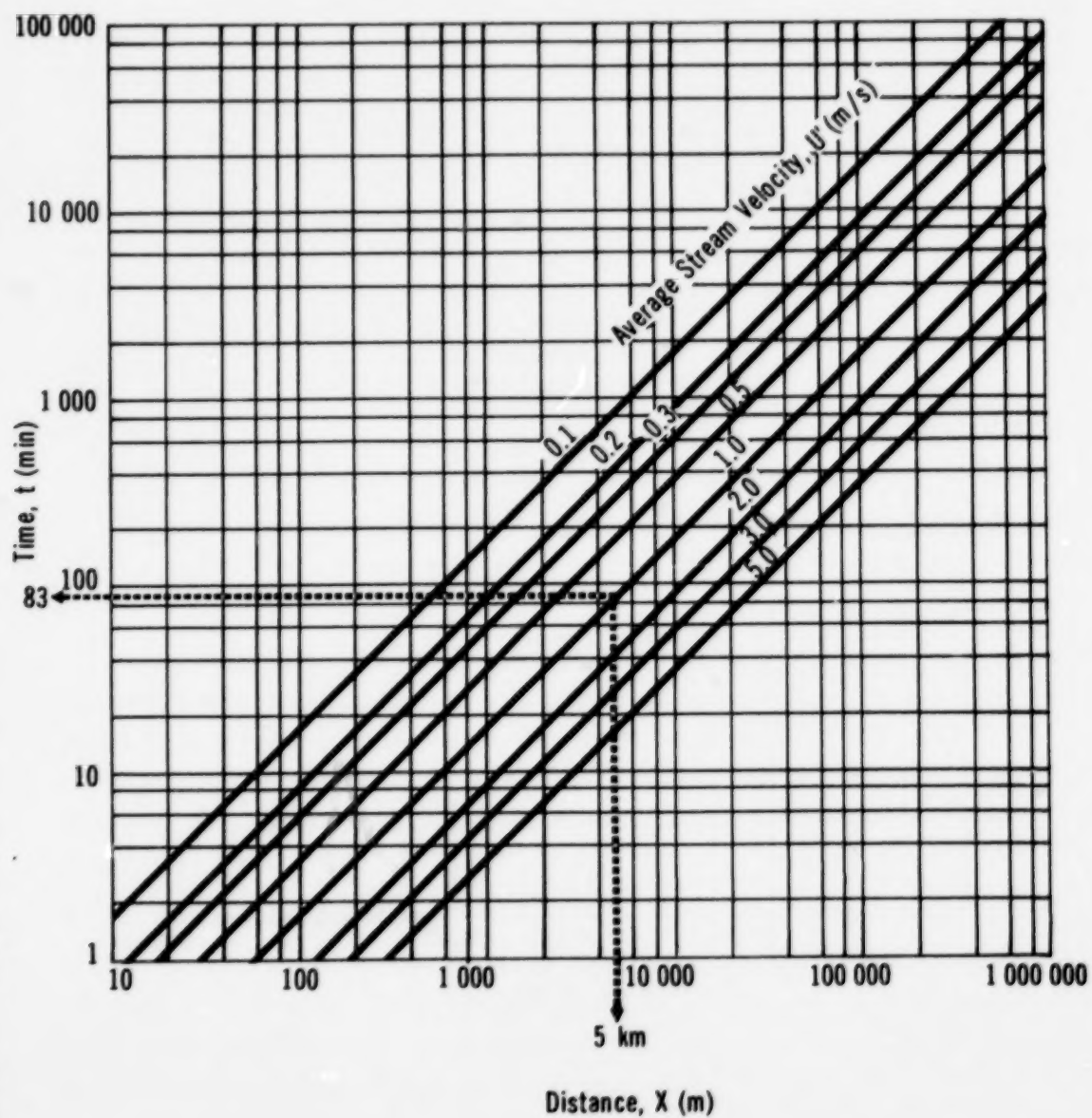
* α and δ are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

UREA

**FLOW CHART TO DETERMINE POLLUTANT
CONCENTRATION IN NON-TIDAL RIVERS**

UREA

TIME vs DISTANCE



UREA

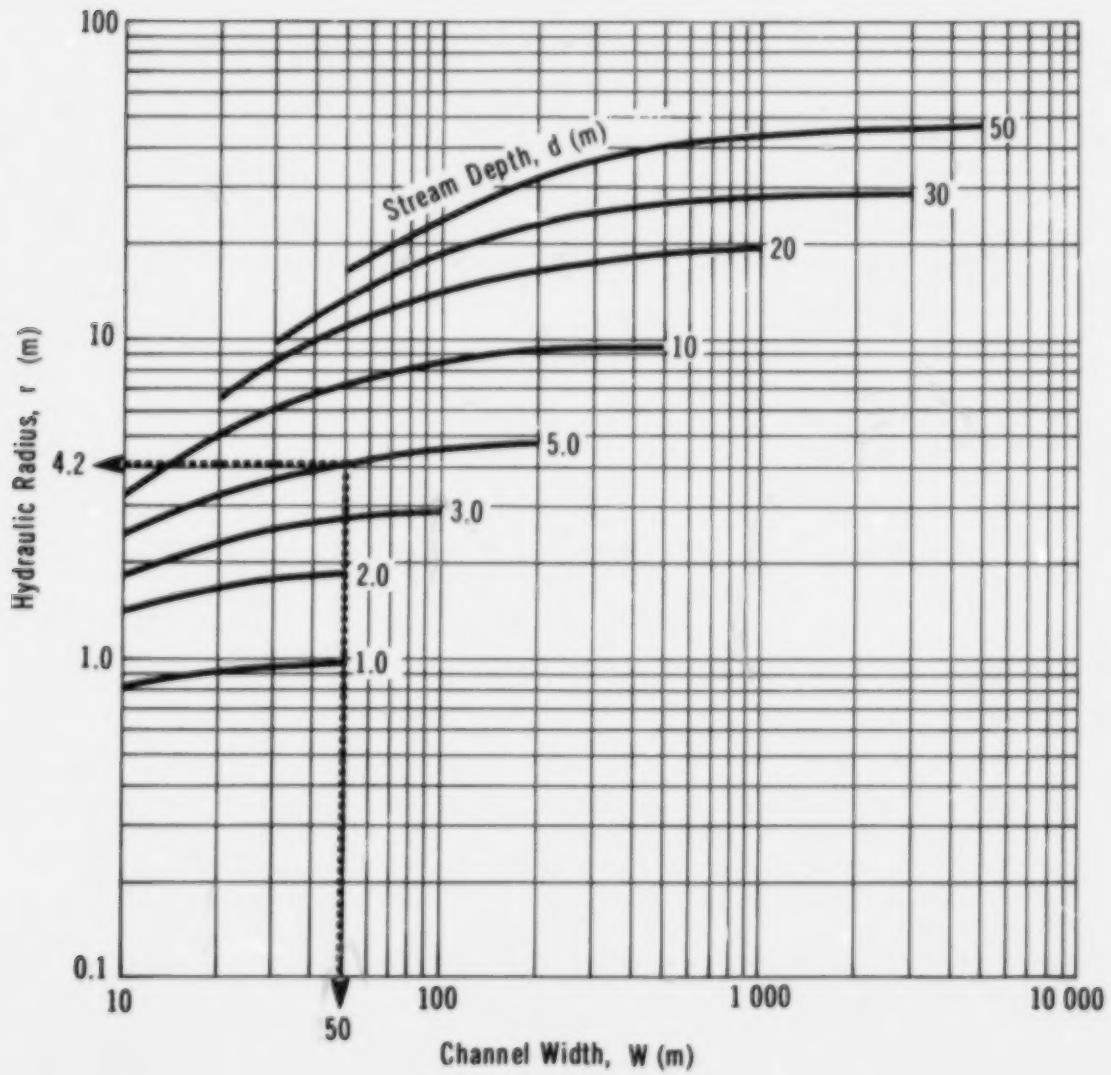
HYDRAULIC RADIUS VS
CHANNEL WIDTH

Figure 13: Diffusion coefficient versus hydraulic radius. Figure 13 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 12 and the average stream velocity (U).

Figure 14: Alpha versus diffusion coefficient. Figure 14 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 15: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 15 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 16: Maximum concentration versus delta. Figure 16 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 16 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

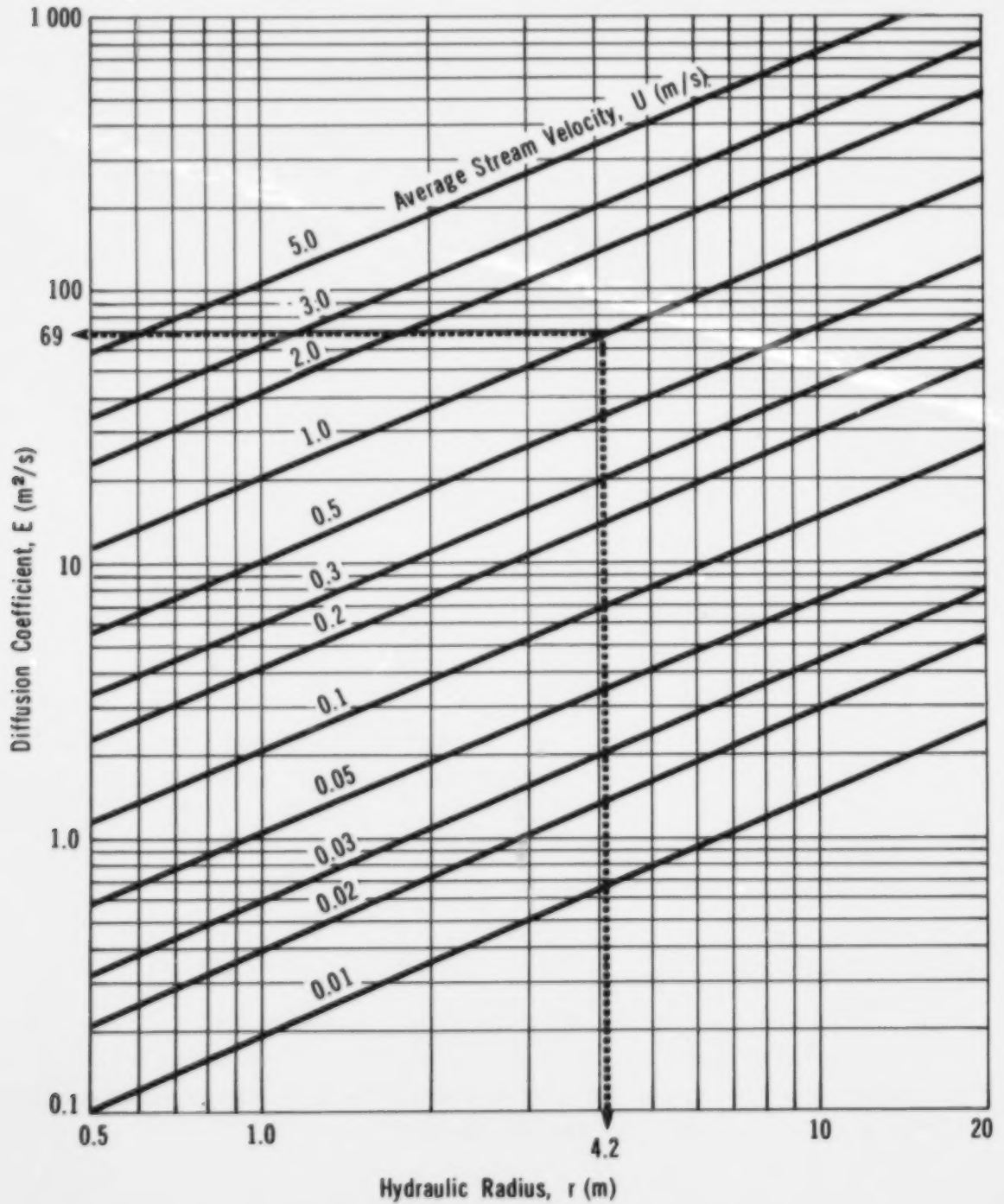
Figure 17: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 17. The radius (r) represents the distance from the spill to the point of interest.

Figure 18: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 18 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

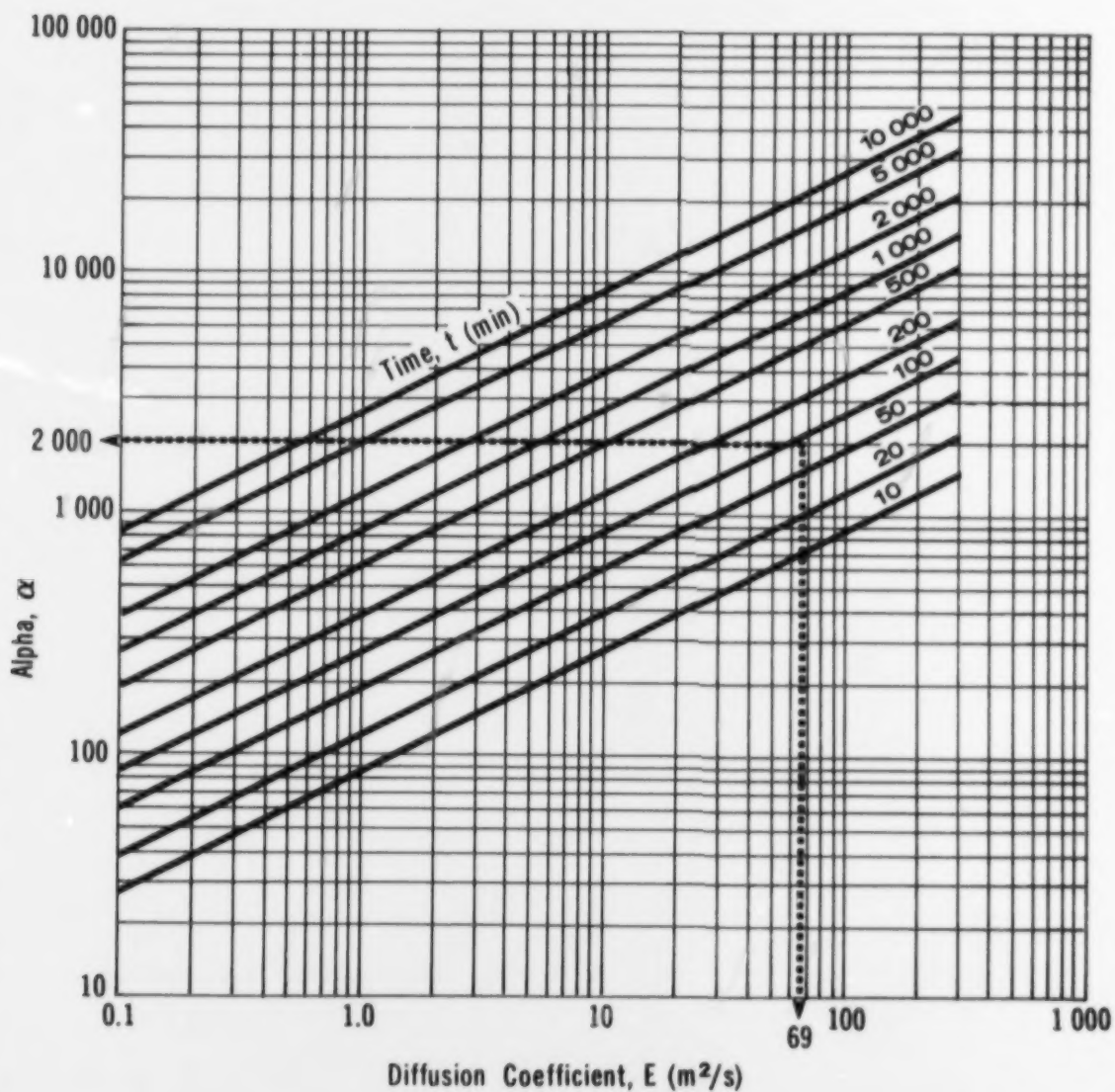
5.4.3.1 Pollutant concentration in non-tidal rivers. A 10 tonne spill of 60 percent urea solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

UREA

DIFFUSION COEFFICIENT
VS HYDRAULIC RADIUS

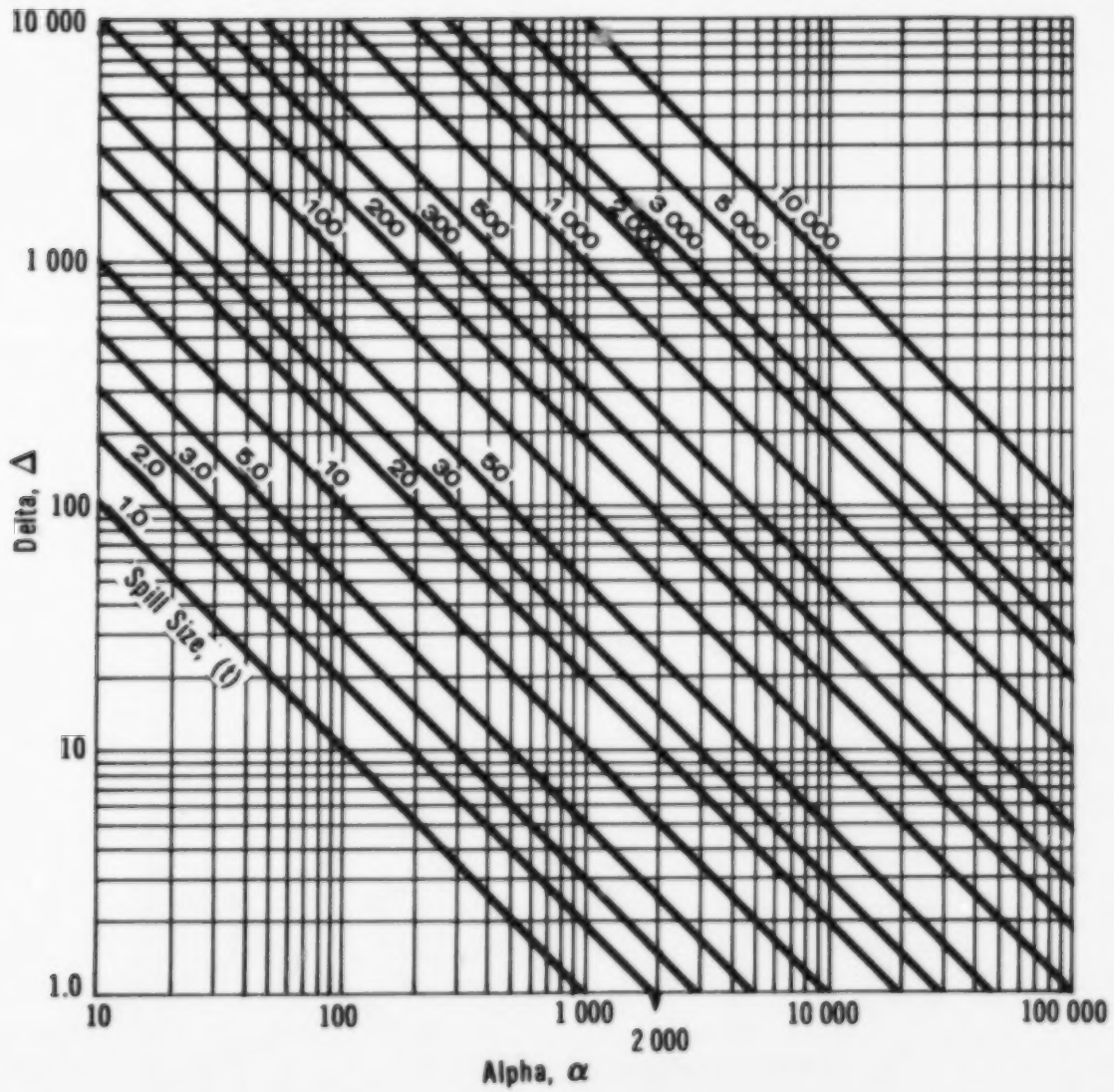
UREA

ALPHA vs DIFFUSION COEFFICIENT



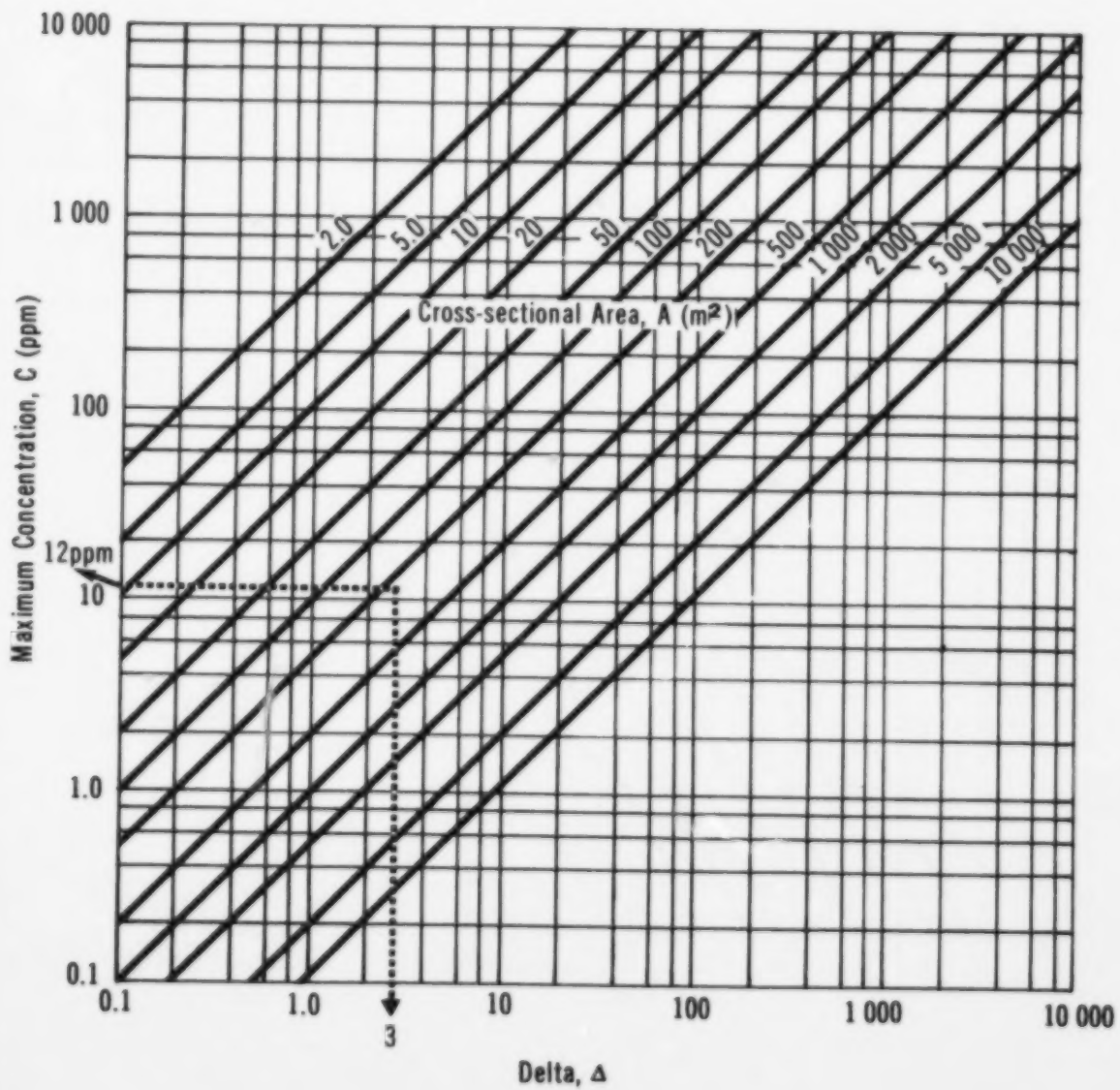
UREA

ALPHA vs DELTA



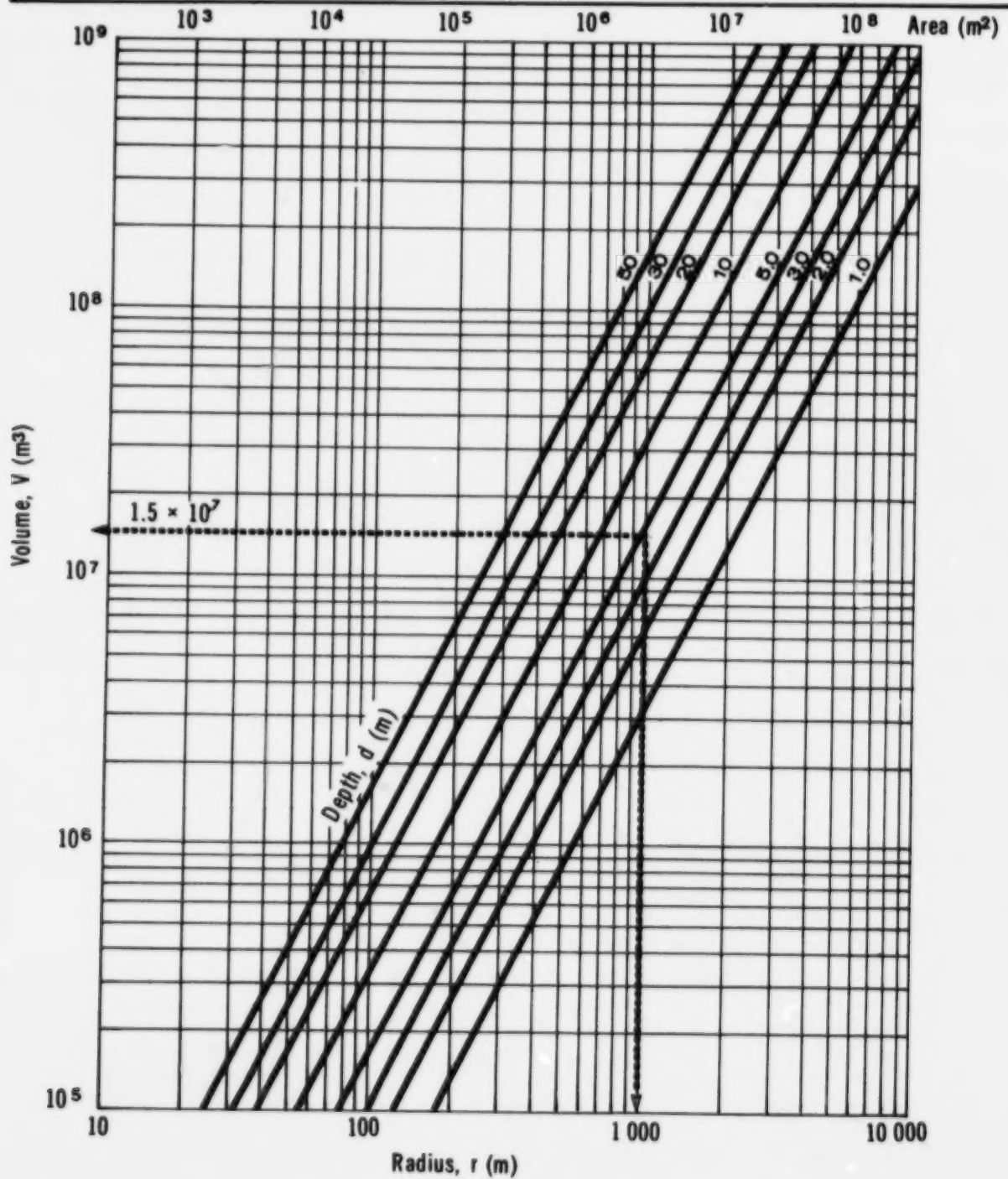
UREA

MAXIMUM CONCENTRATION vs DELTA



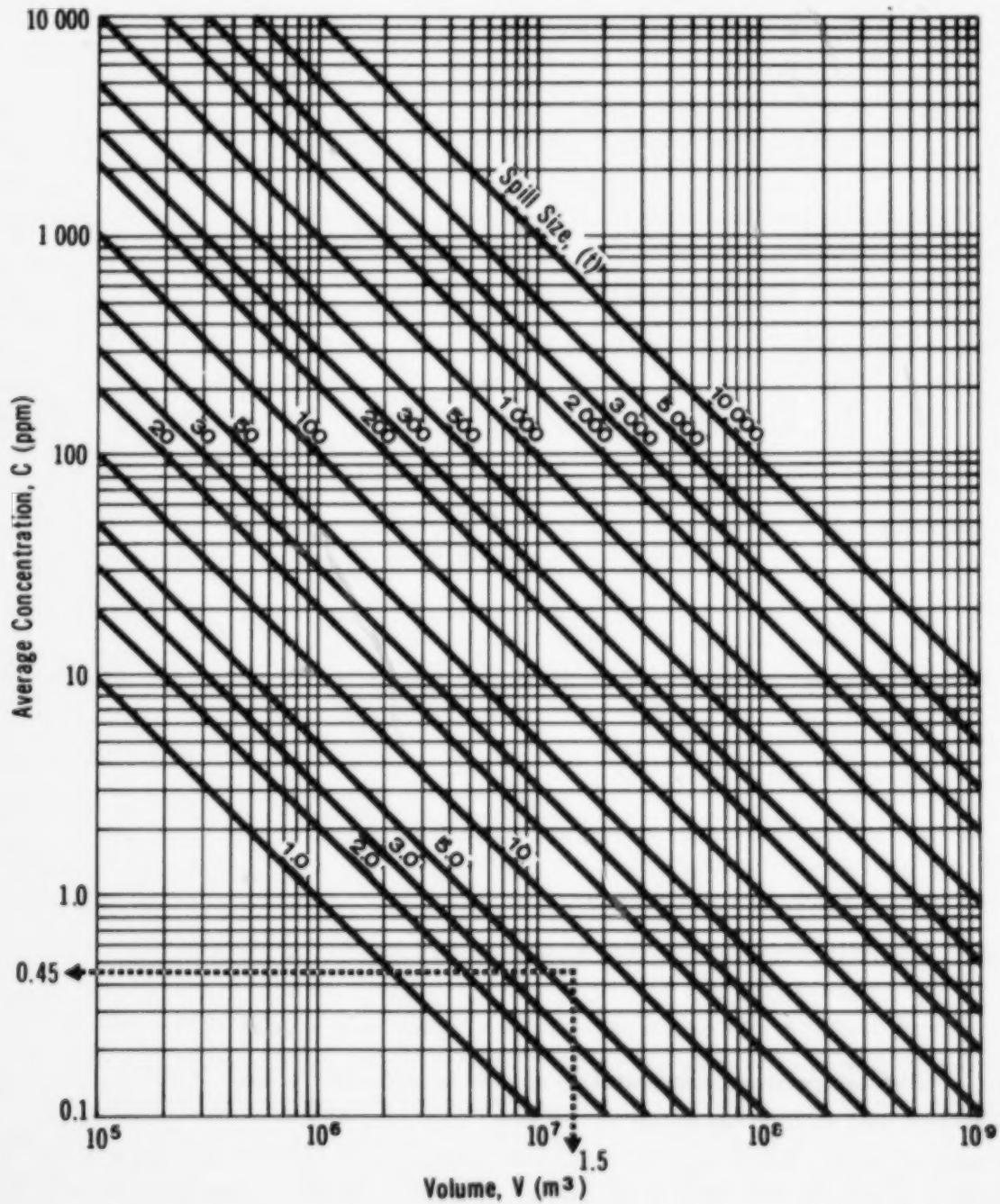
UREA

VOLUME vs RADIUS



UREA

AVERAGE CONCENTRATION vs VOLUME



Solution**Step 1: Define parameters**

- . $W = 50 \text{ m}$
- . $d = 5 \text{ m}$
- . $U = 1 \text{ m/s}$
- . spill mass = 10 tonnes of 60 percent urea solution contains the equivalent of 6 tonnes of urea

Step 2: Calculate the time to reach the point of interest

- . Use Figure 11
- . With $X = 5000 \text{ m}$ and $U = 1 \text{ m/s}$, $t = 83 \text{ min}$

Step 3: Calculate the hydraulic radius (r)

- . Use Figure 12
- . With $W = 50 \text{ m}$ and $d = 5 \text{ m}$, $r = 4.2 \text{ m}$

Step 4: Calculate the longitudinal diffusion coefficient (E)

- . Use Figure 13
- . With $r = 4.2 \text{ m}$ and $U = 1 \text{ m/s}$, $E = 69 \text{ m}^2/\text{s}$

Step 5: Calculate alpha (α)

- . Use Figure 14
- . With $E = 69 \text{ m}^2/\text{s}$ and $t = 83 \text{ min}$, $\alpha = 2000$

Step 6: Calculate delta (Δ)

- . Use Figure 15
- . With $\alpha = 2000$ and spill mass = 6 tonnes, $\Delta = 3$

Step 7: Compute the stream cross-sectional area (A)

- . $A = W \times d = 50 \times 5 = 250 \text{ m}^2$

Step 8: Calculate the maximum concentration (C) at the point of interest

- . Use Figure 16
- . With $\Delta = 3$ and $A = 250 \text{ m}^2$, $C = 12 \text{ ppm}$

5.4.3.2 Average pollutant concentration in lakes or still water bodies. A 10 tonne spill of 60 percent urea solution has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution**Step 1: Define parameters**

- $d = 5 \text{ m}$
- $r = 1000 \text{ m}$
- spill mass = 6 tonnes (equivalent)

Step 2: Determine the volume of water available for dilution

- Use Figure 17
- With $r = 1000 \text{ m}$, $d = 5 \text{ m}$, the volume is approximately $1.5 \times 10^7 \text{ m}^3$

Step 3: Determine the average concentration

- Use Figure 18
- With $V = 1.5 \times 10^7 \text{ m}^3$ and spill mass = 6 tonnes, the average concentration is 0.45 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of urea onto soil and its transport downward through the soil are presented here.

Some urea is conveyed as an aqueous solution although the solid form is more common. When the solid is spilled, only a limited groundwater contamination hazard exists if the soil is dry and if no precipitation falls prior to cleanup. However, if the solution is spilled, or if precipitation or other forms of moisture are present, groundwater contamination can be expected.

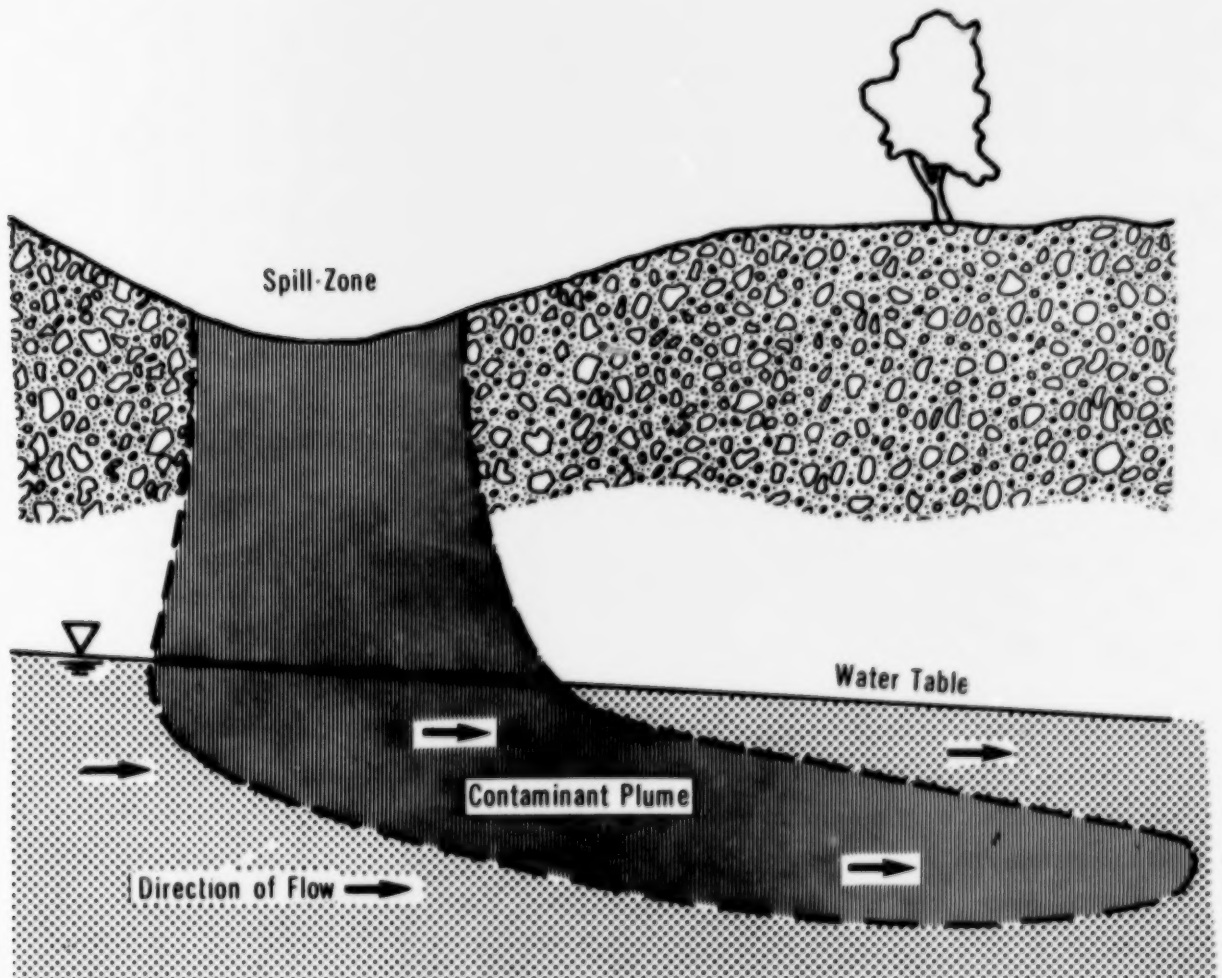
Since urea is very soluble (51.6 g/100 g solution at 20°C), concentrated solutions can infiltrate the soil. Some interaction between urea and the soil will occur. However, much of the urea exchanged ions will migrate downward through the soil.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical may run off into surface water. For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 19.

UREA

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

—Porosity (n) = 0.35

—Intrinsic Permeability (k) = 10^{-9} m^2

—Field Capacity (θ_{fc}) = 0.075

5.5.2 Equations Describing Urea Solution Movement into Soil. The equations and assumptions used to describe contaminant movement in solutions downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Urea Solution in Soil. The saturated hydraulic conductivity (K_0), in m/s, is given by:

$$K_0 = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)
 ρ = mass density of the fluid (kg/m^3)
 μ = absolute viscosity of the fluid ($Pa \cdot s$)
 g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are urea solution (20 percent by weight) and water. The water calculations represent the extreme as the solution is diluted.

Property	Urea (20% by Wt.) 20°C	Water 20°C
Mass density (ρ), kg/m^3	1053	998
Absolute viscosity (μ), $Pa \cdot s$	1.18×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_0), m/s	$(0.87 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils. The Introduction Manual describes the three soils for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of urea solutions into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p .

A flowchart for the use of the nomograms is presented in Figure 20. The nomograms are presented as Figures 21, 22 and 23. The water lines on the nomograms represent the maximum penetration of water at 20°C in time t_p . It is a limiting condition as urea becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of urea has taken place on a silty sand soil. The temperature is 20°C; the spill radius is 8.6 m. A rainfall has occurred. Estimate the depth of urea penetration 8 days after the rain.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20^\circ\text{C}$
- $r = 8.6 \text{ m}$
- Soil = silty sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 8 days

Step 2: Calculate the area of spill

- $A = \pi r^2 = 232 \text{ m}^2$

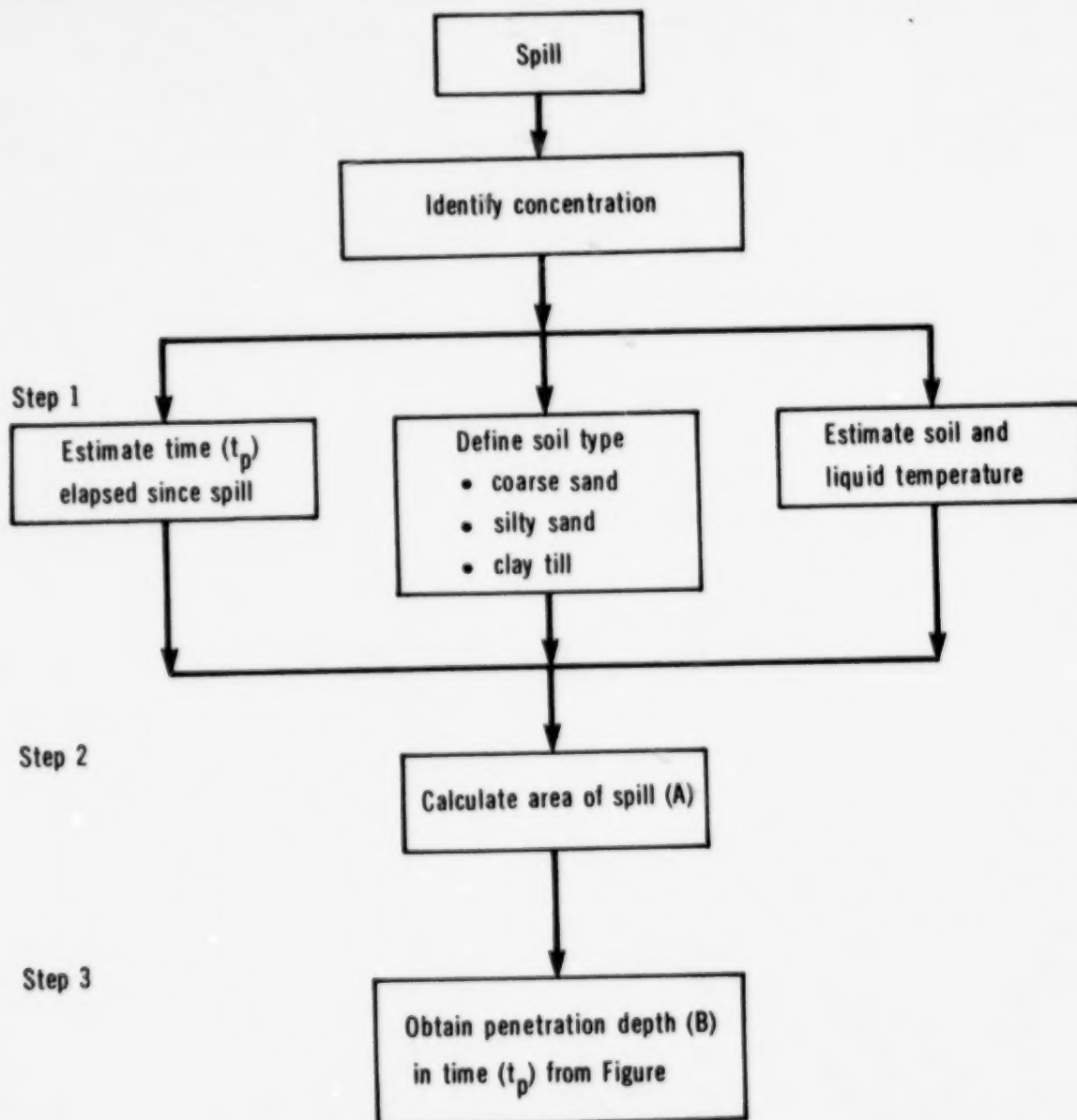
Step 3: Estimate the depth of penetration (B) at time (t_p)

- For silty sand and $t_p = 8$ days, the penetration range is

20% by wt.	Dilute (Water, worst case)
6.0 m	6.7 m
- Groundwater table has not been reached at this point

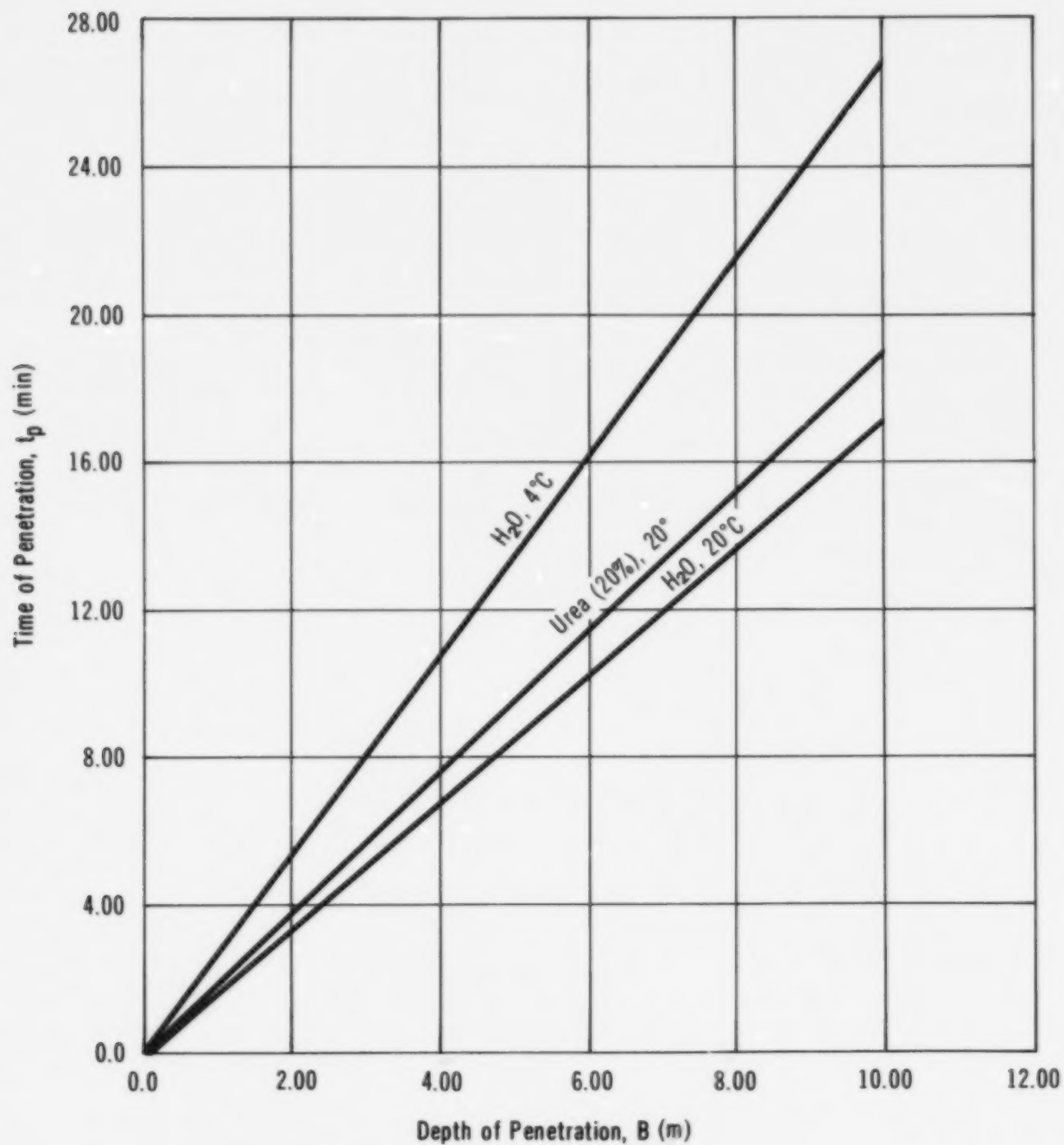
UREA

FLOWCHART FOR NOMOGRAM USE



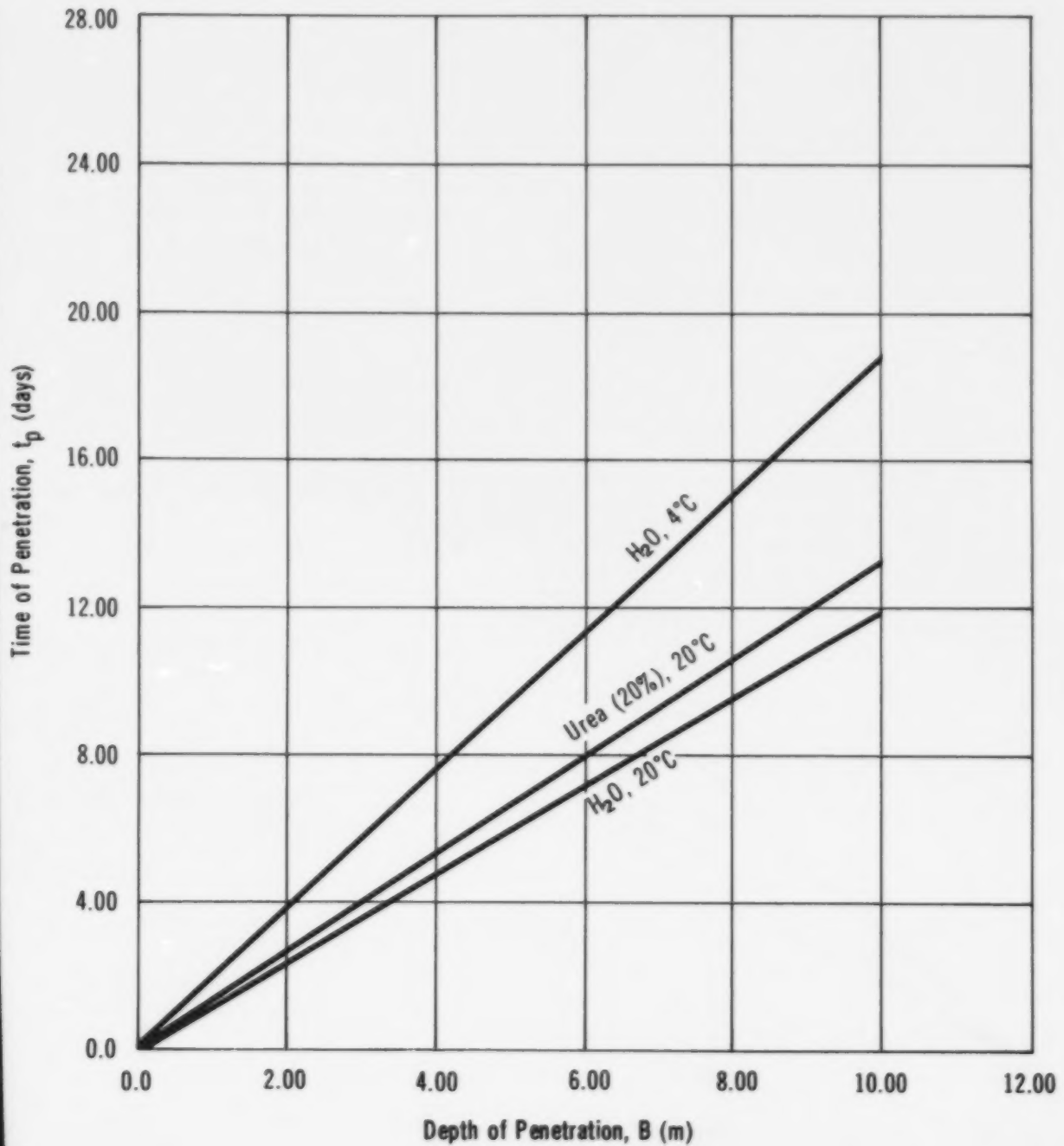
UREA

PENETRATION IN COARSE SAND



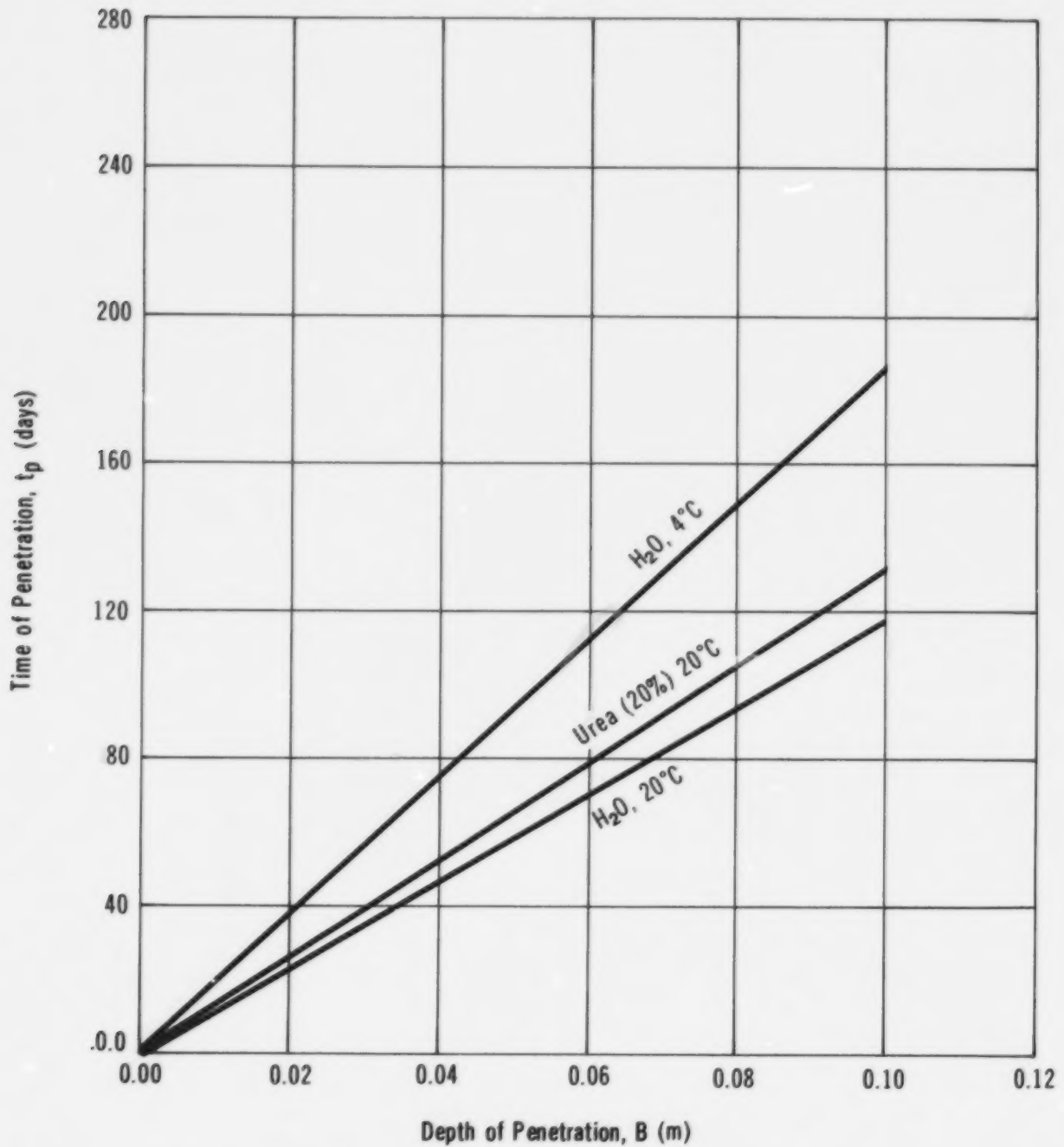
UREA

PENETRATION IN SILTY SAND



UREA

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Drinking Water. The maximum allowable concentration of urea in Class I waters for drinking is 10 mg/L (Verschuere 1984). This is reportedly the maximum concentration producing no organoleptic effects in man (WQCDB-1 1970).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Urea has been assigned a TL_m96 of over 1000 ppm (RTECS 1979).

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
<u>Fish Toxicity Tests</u>					
17.1	24	Minnows	not noticeable	stabilized tap water	WQC 1963
16 000 to 30 000	24	Creek chub	critical range be- low which 4 test fish lived 24 h and above which all died	Detroit River	Gillette 1952
<u>Microorganisms</u>					
>10 000	16	Bacteria (<i>Pseudo- monas putida</i>)	toxic, in- hibit cell multipli- cation	double-dis- tilled water, 25°C	Bringman 1980
>10 000	7 days	Green algae (<i>Scenedesmus qua- dricauda</i>)	toxicity threshold	double-dis- tilled water, 27°C, 50% relative humidity	Bringman 1980
29	72	Protozoa (<i>Entosiphon sulcatum</i>)	toxicity threshold	double-dis- tilled water, 25°C	Bringman 1980

6.3 Mammalian Toxicology

6.3.1 Toxicity.

Conc. (mg/L)	Species	Result	Reference
500	Sheep	LD ₁₀₀ ; mean survival time: 165 min	Edjtehadi 1978
600	Sheep	LD ₁₀₀ ; mean survival time: 109 min	Edjtehadi 1978
750	Sheep	LD ₁₀₀ ; mean survival time: 60 min	Edjtehadi 1978
450 g	Ponies	80% death; oral administration	Clarke 1975
50 g	Goats	80% death within 30 min; oral	Clarke 1975
100 g/day	Sheep	consumption; conc. of urea cannot exceed 6%	Clarke 1975
2000	Adult sheep	continuous convulsions after 165 min	Clarke 1975
2000	Lambs	toxic: died in 90 to 200 min	Clarke 1975
450	Cattle	toxic dose; given first time	Clarke 1975
50 g	Cattle	poisoning (min. first dose)	Clarke 1975
100 to 200 g	Cattle	increasing dose at various time; no ill effect	Clarke 1975

Cattle quickly develop tolerance to urea doses, but such tolerance is readily lost if urea is withheld a few days. Poisoning of cattle has resulted from eating grass where urea fertilizer was spread unevenly on pasture (Clarke 1975).

6.4 Other Land and Air Toxicity

Conc. (mg/L)	Species	Result	Reference
600	Frogs	LD _{LO} , subcutaneous	RTECS 1979
16 000	Pigeons	LD _{LO} , subcutaneous	RTECS 1979

6.5 Fate and Effect Studies

The effect of urea on blood constituents of the Indian catfish (*Meteropheustes fossilis*) was studied; relatively high levels were required to produce an imbalance (Srivastava 1982).

In a trial of urea fertilization of an estuary for the purposes of increasing salmonid food items, it was found that the fertilization did not accelerate primary productivity or nitrogen regeneration. It was concluded that the fertilizer did not result in any appreciable enhancement of juvenile salmonid growth or survival (Stockner 1982).

Algal growth in rice fields was examined at 25 and 50 mg/L (as N) urea added to cultures of *Bracteacoccus minor*, *Scenedesmus* sp. and *Chlamydomonas* sp. Growth was accelerated by the addition but there was no significant difference between the 25 mg/L and 50 mg/L test groups (Barrett 1982).

Urea fertilizer was applied to a pasture and runoffs were measured. Maximum concentration of runoff was attained for ammonia nitrogen 3 weeks after application and for nitrate nitrogen 1 week after application. In the runoff, ammonia-nitrogen was only 0.3 percent of that applied, nitrogen nitrate was 1.0 percent, and total nitrogen was 7.1 percent of that applied. It was concluded that most applied urea will not run off (Sharpley 1983).

A forest fertilization study led to the conclusion that application rates less than 224 kg/ha (200 lb. N/acre) were ineffective in supplying nitrogen. Urea applications above this threshold brought about increases in soil nitrogen, pH, absorbed ammonia and cation exchange capacity, the latter especially in surface and litter material. Addition of urea appeared to have adverse effects on the uptake of phosphorus (Baker 1970).

6.6 Degradation

Degradation Rate	Species	Water Conditions	Reference
max. 11.6 mg/L/h, ave. 10.9 mg/L/h	psychrophilic bacteria	waste water treatment at 20°C	Verschueren 1984
max. 4.0 mg/L/h, ave. 3.2 mg/L/h	psychrophilic bacteria	waste water treatment at 2°C	Verschueren 1984

Conc. (mg/L)	Time (days)	Effect	Water Conditions	Reference
1 to 15	up to 14	degradation negligible	< 8°C, river water	Evans 1973
1 to 15	4 to 6	degradation complete	20°C, river water	Evans 1973

6.7 Long-term Fate and Effects

Urea will degrade to ammonia and eventually to nitrate. By providing a nitrogen source, it can enhance eutrophication (OHM-TADS 1981).

7 HUMAN HEALTH

There is little information in the published literature concerning the toxicological effects of test animal and human exposures to urea. Urea has been tested for mutagenicity and carcinogenicity. The NCI bioassay is reported as producing insufficient data to draw conclusions concerning the carcinogenic potential of urea (RTECS 1979). No data were found concerning the chemical's potential teratogenic effects. No toxicity reviews of urea were found in the literature. Urea has been reported in the EPA TSCA Inventory.

The toxicology data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

No recommended exposure limits for urea were found in the literature.

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
22 mg (3 d, intermittently)	Mild irritation.	RTECS 1979
SPECIES: Guinea Pig		
Unspecified	Treatment of guinea pigs with urea increased the effects of the subsequent sensitization with epoxy resins. Urea treatment increases the percentage of animals sensitized by epoxy resins from 50 to 87 percent. Urea alone did not sensitize skin.	TDB (on-line) 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	When the urea concentration is higher in blood than in the eye, there is movement of water from eye to blood stream, reducing the volume of both the vitreous and aqueous humors and lowering intraocular pressure. When the concentration in the blood drops below that in the eye, water may move into the vitreous, pushing the lens forward and consequently increasing the risk of angle-closure glaucoma.	TDB (on-line) 1981
Unspecified	The eye is permeable to urea. A rebound elevation in intraocular pressure and vitreous volume may occur after ocular hypotensive effect has terminated (about 8 to 12 hours after administration).	TDB (on-line) 1981
SPECIES: Rabbit		
0.2 mL of 10 M solution	When injected into the vitreous humor of rabbits, has caused inflammation.	TDB (on-line) 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour characteristics: Odourless or faint ammonia-like odour (CHRIS 1978).

7.3.2 Taste.

Parameter	Media	Concentration	Reference
Taste Recognition Threshold	in water	0.0501 moles/L (3 ppm)	ASTM 1980
Taste Detection Threshold	in water	0.120 moles/L (7 ppm)	ASTM 1980

Parameter	Media	Concentration	Reference
Taste Recognition Threshold	in water	0.261 moles/L (16 ppm)	ASTM 1980
Taste Recognition Threshold	in water	0.316 moles/L (19 ppm)	ASTM 1980
Taste Recognition Threshold	in water	0.398 moles/L (24 ppm)	ASTM 1980

7.4 Toxicity Studies

7.4.1 Inhalation. No data.

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
<u>Acute Exposure</u>		
SPECIES: Domestic Cattle		
511 mg/kg	LD ₅₀	RTECS 1979
SPECIES: Sheep		
2 g/kg	Lambs died in 90 to 200 minutes. Adult sheep exhibited almost continuous convulsions after 165 minutes. Sheep can consume up to 100 grams of urea a day, provided that the concentration of urea in ration does not exceed 6 percent. Liver dysfunction increases the susceptibility to poisoning.	TDB (on-line) 1981
SPECIES: Goat		
50 g	Killed 4 out of 5 goats within 30 minutes.	TDB (on-line) 1981
SPECIES: Ponies		
450 g	Killed 7 out of 8 ponies.	TDB (on-line) 1981

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Pig		
16 g/kg	LD _{LO}	RTECS 1979
SPECIES: Dog		
3000 mg/kg	LD _{LO}	RTECS 1979
SPECIES: Rabbit		
3000 mg/kg	LD _{LO}	RTECS 1979

7.4.4 Mutagenicity and Carcinogenicity.

Exposure Level (and duration)	Effects	Reference
SPECIES: Hamster		
16 g/L (24 h)	Cytogenic analysis for chromosomal aberrations in hamster fibroblast cells.	RTECS 1979
Unspecified	N.C.I. carcinogenesis assay has been completed. No report was made due to insufficient data.	RTECS 1979

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 **Inhalation.** No data.

7.5.2 **Ingestion.** No data.

7.5.3 **Skin.**

1. Mild irritation (RTECS 1979).

7.5.4 Eyes.

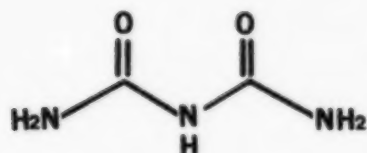
1. Irritation (CHRIS 1978).
2. Changes in intraocular pressure (TDB (on-line) 1981).

7.6 Human Toxicity to Decay or Combustion Products

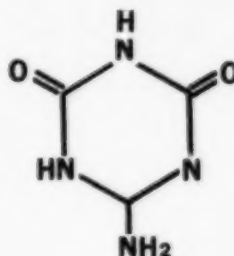
Urea decomposes at atmospheric pressure and at its melting point to ammonia, biuret, cyanuric acid, ammeline and triuret (Kirk-Othmer 1983).

Ammonia is a colourless gas with a penetrating, pungent and suffocating odour. It is detectable by odour at concentrations as low as 5 ppm. At 100 ppm, irritation of mucous membranes becomes noticeable; prolonged exposure to concentrations above 400 ppm may destroy mucous surfaces by dissolving or emulsifying keratin, fat, and cholesterol. The most frequent cause of death from exposure to ammonia is pulmonary edema. Its TLV[®] is 25 ppm (8 h - TWA) and the STEL is 35 ppm (TLV 1983).

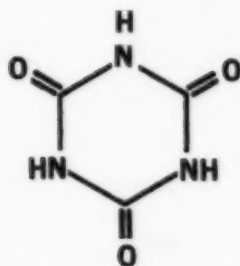
Little information is available on the toxicity of biuret, cyanuric acid, ammeline and triuret (all shown below).



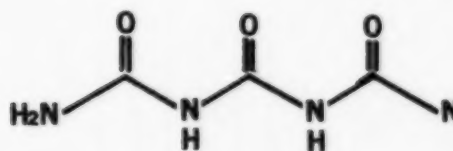
biuret



ammeline



cyanuric acid



triuret

8

CHEMICAL COMPATIBILITY

8.1

Compatibility of Urea with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	DECOMPOSITION	FORMATION OF TOXIC FUMES	PRESSURIZATION OF SUBSTANCES OF GREATER TOXICITY VESSELS	SOLUBILIZATION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>GENERAL</u>											
Fire				•						If temperature exceeds the boiling point.	Sax 1979
Heat				•						When heated above the boiling point.	Sax 1979
<u>SPECIFIC CHEMICALS</u>											
Chromyl Chloride	•										Bretherick 1979
Gallium Perchlorate				•			•			The salt decomposes violently on heating.	NFPA 1978
Nitrosyl Perchlorate	•										Bretherick 1979
Sodium Nitrite		•									Bretherick 1979
Titanium Tetrachloride				•						The liquid hexaurea complex formed decomposes violently at above 90°C.	Bretherick 1979

8.1

Compatibility of Urea with Other Chemicals and Chemical Groups
 (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
<u>CHEMICAL GROUPS</u>													
Hypochlorites		•								Nitrogen tri- chloride is formed; it ex- plodes spon- taneously in air.			NFPA 1978

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Urea is a nonflammable solid; it may become slightly dangerous when heated to its decomposition temperature (133°C) (Sherritt MSDS 1980).

9.1.2 Fire Extinguishing Agents. Most fire extinguishing agents may be used in fires involving urea.

9.1.3 Spill Actions, Cleanup and Treatment.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact (Olin MSDS 1981).

9.1.3.2 Spills on land. For spills of solid urea, shovel contaminated material into containers for disposal (Olin MSDS 1981). For spills of urea in solution form, contain if possible by forming mechanical and/or chemical barriers to prevent spreading. Neutralize with vinegar or dilute acid (EPA 670/2-75-042).

9.1.3.3 Spills in water. Contain if possible. Apply activated carbon at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Use mechanical dredge or lifts to remove the immobilized masses of pollutants (EPA 670/2-75-042).

The following sorbent materials may be used in spill situations: Amberlite XAD resins, Dowex 50WX8, and Amberlite IRA 900 (CG-D-38-76).

9.1.4 Treatment and Disposal. Production plants may have a number of treatment processes in place; recovered urea-contaminated water may be passed to them (Bruls 1982). Urea also degrades in standard sewage plants at temperatures around 20°C so this option may also be used.

Reverse osmosis has been tested on urea solutions. Cellulose acetate membranes removed 20-40 percent of urea in a single pass, cross-linked polyethylenimine removed 70-80 percent, and aromatic polyamide membranes removed 30 to 50 percent (Fang 1976).

In the event that the collected material is not contaminated with hazardous chemicals, the urea can be spread as a fertilizer; rates of 200-400 kg/ha are recommended.

9.1.5 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be urea:

- Safety goggles, coveralls, impervious gloves and boots should be worn (Olin MSDS 1981).
- If intense heat prevails, a cannister (organic and acid gas) mask should be worn (OHM-TADS 1981).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Detection of Urea in Air

Since urea is nonvolatile and is generally shipped in pellet form, contamination of the air would not be expected in the event of a spill.

11.2 Quantitative Method for the Detection of Urea in Water

11.2.1 Microcoulometry (ASTM 1979). Urea in water may be determined as total nitrogen in concentrations from 0.5 to 100 mg/L.

A minimum volume of 2 L of representative sample is collected in an appropriate container. A 3 μ L aliquot of sample is injected into a stream of hydrogen gas flowing at 300 mL/min through a quartz pyrolysis tube. The pyrolysis tube contains granular 10/40 mesh nickel and is housed in a pyrolysis furnace with three separate heat zones, capable of reaching the following temperatures: inlet zone, 700°C; pyrolysis zone, 800°C; and outlet zone, 800°C. The pyrolysis tube should also have 50 percent sodium hydroxide on asbestos at the outlet to serve as an acid gas scrubber. The titration cell contains a sensor-reference pair of electrodes and a stirrer set to produce a slight vortex. The microcoulometer has variable attenuation and bias voltage set at 110 mV with a gain of 400 to 600.

The sample concentration is determined by a suitable electronic integrator in conjunction with a calibration curve.

11.3 Qualitative Method for the Detection of Urea in Water

The sample is collected as in Section 11.2.1. Urea may be determined qualitatively by reaction with nitrous acid. A suitable volume of sample is placed in a test tube and nitrous acid is added. The evolution of carbon dioxide indicates the presence of urea (Morrison 1976).

11.4 Quantitative Method for the Detection of Urea in Soil

11.4.1 Spectrophotometric (Mulvaney 1979). Concentrations up to 100 µg/mL of urea in soil may be determined by spectrophotometric measurement.

A soil sample is extracted with 2 M potassium chloride-phenyl-mercuric acetate solution. A 10 mL volume of extract is transferred to a 50 mL volumetric flask and diluted with 10 mL of 2 M potassium chloride-phenylmercuric acetate. A 30 mL volume of colour reagent is added to the mixture. The reagent is prepared by mixing 50 mL of diacetyl monoxime (2.5 g/100 mL) and 30 mL of thiosemicarbazide (0.25 g/100 mL) and diluting to 1 L with acid reagent. The acid reagent is prepared by mixing 40 mL of concentrated sulphuric acid and 1 L of 85 percent w/w phosphoric acid and diluting to 2 L with distilled water. The colour reagent must be prepared immediately before use.

The sample treatment continues as follows. After the addition of the colour reagent, the mixture is swirled and placed in a water bath for 30 minutes at 85°C. The sample is then water-cooled and made up to 50 mL if sample loss has occurred. The sample absorbance is determined at 527 nm using a suitable spectrophotometer. The sample concentration is determined using a calibration curve.

11.5 Qualitative Method for the Detection of Urea in Soil

The sample is collected as in Section 11.4.1. Urea may be determined qualitatively by reaction with nitrous acid. A suitable volume of sample is placed in a test tube and nitrous acid is added. The evolution of carbon dioxide indicates the presence of urea (Morrison 1976).

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EnviroTIPS
Common Abbreviations

BOD	biological oxygen demand	*Be	degrees Baumé (density)
b.p.	boiling point	MMAD	mass median aerodynamic diameter
CC	closed cup	MMD	mass median diameter
cm	centimetre	m.p.	melting point
CMD	count median diameter	MW	molecular weight
COD	chemical oxygen demand	N	newton
conc	concentration	NAS	National Academy of Sciences
c.t.	critical temperature	NFPA	National Fire Protection Association
eV	electron volt	NIOSH	National Institute for Occupational Safety and Health
g	gram		
ha	hectare		
Hg	mercury		
IDLH	immediately dangerous to life and health	nm	nanometre
Imp. gal.	imperial gallon	o	ortho
in.	inch	OC	open cup
J	joule	p	para
kg	kilogram	P _c	critical pressure
kJ	kilojoule	PEL	permissible exposure level
km	kilometre	pH	measure of acidity/alkalinity
kPa	kilopascal	ppb	parts per billion
kt	kilotonne	ppm	parts per million
L	litre	P _s	standard pressure
lb.	pound	psi	pounds per square inch
LC ₅₀	lethal concentration fifty	s	second
LC _{LO}	lethal concentration low	STEL	short-term exposure limit
LD ₅₀	lethal dose fifty	STIL	short-term inhalation limit
LD _{LO}	lethal dose low	T _c	critical temperature
LEL	lower explosive limit	TC _{LO}	toxic concentration low
LFL	lower flammability limit	Td	decomposition temperature
m	metre	TD _{LO}	toxic dose low
m	meta	TL _m	median tolerance limit
M	molar	TLV	Threshold Limit Value
MAC	maximum acceptable concentration	Ts	standard temperature
max	maximum	TWA	time weighted average
mg	milligram	UEL	upper explosive limit
MIC	maximum immission concentration	UFL	upper flammability limit
min	minute or minimum	VMD	volume mean diameter
mm	millimetre	v/v	volume per volume
µg	microgram	w/w	weight per weight
µm	micrometre		